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p. 385, last line, read: be called the "physiological soil solution," etc.
p. 386, 27th line, read: the weight of those produced in a good soil, etc.



THE LIBERATION OF POTASSIUM FROM FELDSPARS, AND OF POTASSIUM AND CARBON DIOXIDE FROM SOILS BY FERTILIZER AND ACID TREATMENTS¹

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Although many cultivated soils are abundantly supplied with potassium, various field crops have often been benefited by small applications of soluble potassium fertilizers. This fact gives evidence that in many cases there is a deficiency of available potassium for maximum crop production. It also indicates the lack of understanding of the conditions necessary for the liberation of potassium in soils from its insoluble forms.

The literature on the solubility of soil potassium is highly confusing and contradictory, but investigators generally agree that certain agencies must be constantly and vigorously active in liberating unavailable soil potassium. Carbon dioxide is one of the chief agents which according to Greaves, (14) reacts with the insoluble potassium silicates to form soluble potassium carbonate.

Ames (1) believes that the salts formed as a result of the acidity produced by bacterial and chemical action effect the liberation of potassium rather than the acids themselves.

There is also the contention of Fraps (12) and Hopkins and Aumer (15) that decaying organic matter has the power to liberate insoluble soil potassium.

Other investigators claim that the application of certain fertilizers and neutral salts bring soil potassium into solution.

Most of these theories, however, are not based upon facts established by experimental data. Therefore, the need for a more complete study of the subject is plainly evident. A thorough understanding of the various agencies involved is absolutely essential in order to formulate any scheme of soil treatments which will permit profitable and economical use of the abundant supply of native soil potassium. Carbon dioxide, bacterial activities, mineral and organic acid, and decaying organic matter may all be expected to exercise some influence in making soil potassium available. The experiments reported in this paper were planned in an attempt to ascertain the relative effect of these various factors on the liberation of potassium from the insoluble supply in the soil.

¹ Part of a thesis submitted to the Faculty of the Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² The writer wishes to express his appreciation to Dr. P. E. Brown for the suggestions and criticism given concerning the work and the manuscript, and to Drs. Paul Emerson and H. W. Johnson for the suggestions and help given during the course of this work.

PART I

Experiments in solutions

This experiment was designed to study certain non-biological factors which might show some effect on the solubility of potassium in potassium-bearing minerals such as orthoclase, KAlSi_3O_8 , and alunite, $\text{K}(\text{Al}(\text{OH})_2)_2(\text{SO}_4)_2$.

The orthoclase was obtained from rocks collected locally. These were crushed and ground to pass through a sixty mesh sieve. The alunite was secured from the Mineral Products Corporation, Maryvale, Utah, and ground to the same fineness as the orthoclase. Upon analyses the orthoclase showed a total potassium content of 3.65 per cent; the alunite, 3.92 per cent. One hundred-gram portions of orthoclase or alunite, or mixtures of the two were used with varying treatments.

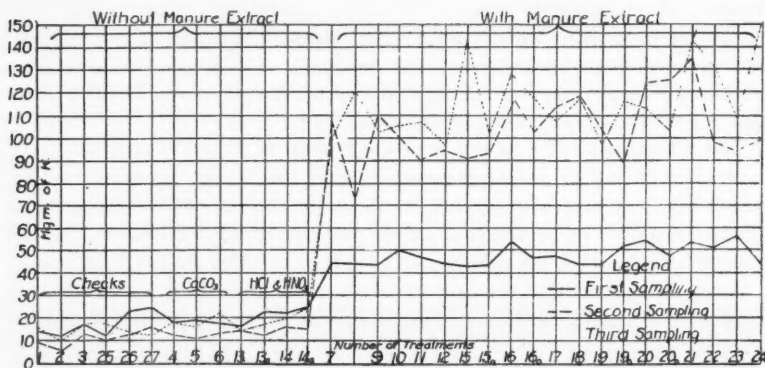


FIG. 1. GRAPH SHOWING THE EFFECT OF MANURE EXTRACT AND ACID TREATMENTS ON SOLUTIONS CONTAINING ORTHOCLASE AND ALUNITE

The treatments included manure extract, lime, gypsum and certain acid treatments. The manure extract was prepared by mixing 1000 gm. of air-dry, partly decomposed barnyard manure with 6 liters of distilled water, after standing for 4 hours the manure infusion was filtered through coarse filter paper. Fifty cubic centimeters of the filtrate were used for the treatments. This amount upon analysis showed a content of 76.8 mgm. of potassium. CaCO_3 and CaSO_4 were added in 2 gm. quantities. Hydrochloric, nitric and citric acids were used. One per cent of citric acid was added, and sufficient amounts of hydrochloric and nitric acids were used so that after the various ingredients were added the titration showed an acidity equivalent to a desired normality of the particular acid.

The mixtures of alunite and orthoclase with the various treatments were placed in shaker bottles, made up to 500 cc. with distilled water and then sterilized in the autoclave for thirty minutes at fifteen pounds pressure. In order to insure proper mixing all the bottles were shaken for 10 hours in the shaking machine before they were placed in the incubator where they were kept at a constant temperature of 25°C.

The arrangement of the experiment is shown in table 1. In order to determine the effect of sterilization, mixtures 25, 26 and 27 and those marked "a" were not sterilized. Mixtures 25, 26, 27 were prepared just previous to the first sampling for the purpose of determining the water-soluble potassium of the minerals. The samplings were taken at intervals of

four and eight weeks. At each sampling the bottles were shaken for thirty minutes. Then 100 cc. were quickly taken out with continuous stirring in order to keep the solids and liquids in the original proportions. The samples were filtered and 50 cc.-aliquots were used for water-soluble potassium determinations. The results of the three samplings calculated in milligrams on the basis of 500 cc. of solution are given in table 1. Figure 1 presents graphically the results of the three samplings.

The potassium added in the manure extract and the amount obtained before incubation of the checks are water-soluble forms and must be deducted from the total results. Since the checks did not change to any appreciable extent during the course of the experiment, the results of the three determinations on the six checks were averaged and used as the water-soluble amount present in the minerals.

Table 1 indicates that the manure extract had a large effect on the solubility of the potassium in orthoclase and alunite after 16 weeks of incubation. This supports the belief that decaying organic matter liberates potassium from potassium-bearing minerals. If the average amount liberated by the addition of CaCO_3 is deducted from the surplus due to the manure extract and CaCO_3 , and if the total average potassium present in orthoclase and alunite is taken as a mean, it is found that 0.195 per cent of the total potassium was liberated through the effect of the manure extract.

The effects of CaCO_3 and CaSO_4 were comparatively small and the data show also that the minerals were not acted upon by the acids, thus supporting the observations of McCaughy and Fry (20) who claim that acids do not affect orthoclase. However, the combined action of manure extract and acids in certain concentrations is quite remarkable. The manure extract with 1.0 *N* HNO_3 and 0.1 *N* HCl apparently had no effect, but with the weaker concentrations of HCl and HNO_3 , and with citric acid there were large effects. These are best indicated in figure 2 where averages of the result for each treatment have been plotted in the order of their increasing effect.

McCall and Smith (19) found that in composting greensand with manure and sulfur, it seemed necessary for a certain degree of acidity to be developed before any appreciable amount of potassium was made water-soluble, thus confirming the observations made here. The results are also substantiated by Ames and Boltz (2) and more recently by Ames (1), who contended, however, that the effect of the acidity was due to salts formed from the acids rather than to the direct action of the acids. This idea appears to find support in these results for the acids by themselves showed no appreciable effect on the minerals.

The behavior of the solutions during the first 4-week period of the experiment is of particular interest, because it demonstrated the phenomenon of absorption. Although the figures in the first column of the table show an apparent increase where manure extract was applied, a considerable decrease was really secured as indicated by the minus sign in the second column where the water-soluble potassium applied in the form of manure extract and feldspars was deducted. Evidently potassium bearing minerals absorb potassium from solutions. This was also observed by DeTurk (8). If this fact is taken into account the increases due to the manure extract as reported in the table

TABLE 1
Water-soluble potassium liberated from orthoclase and alunite computed for 500 cc. solutions

SAMPLE NUMBER	MATERIAL USED	TREATMENT	K IN FIL-TRATE 10/20/21	GAIN OR LOSS DUE TO TREATMENT	K IN FILTRATE 11/21/21	GAIN OR LOSS DUE TO TREATMENT	K IN FILTRATE 1/21/22	GAIN OR LOSS DUE TO TREATMENT	REACTION
			mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	pH
1	Orth.		13.8		9.8		15.3		8.8
2	Alun.		11.4	Check*	6.2		10.1	Check*	7.5
3	Mix.		17.7		12.8		19.0		8.5
4	Orth.	CaCO ₃	18.2	+4.7	12.4	-1.1	18.6	+5.1	8.8
5	Alun.		19.0	+5.5	10.6	-2.9	17.3	+3.8	8.7
6	Mix.		18.0	+4.5	14.3	+0.8	22.7	+9.2	8.4
7	Orth.	CaCO ₃ + manure extract*	45.9	-44.4	104.7	+14.4	101.9	+11.6	8.8
8	Alun.		45.9	-44.4	70.7	-19.6	120.6	+30.3	8.7
9	Mix.		43.6	-46.7	111.8	+21.5	101.6	+11.3	8.4
10	Orth.	CaSO ₄ + manure extract	50.2	-40.1	100.2	+9.9	107.6	+17.3	8.6
11	Alun.		48.8	-41.5	91.3	+1.0	108.7	+18.4	8.5
12	Mix.		44.4	-45.9	94.1	+3.8	96.0	+5.7	8.6
13	Orth.	CaCO ₃ + 0.01 N HCl	17.7	+4.2	15.3	+1.8	15.4	+1.9	4.4
13a	Alun.		22.0	+8.5	11.9	-1.6	16.2	+2.7	3.1
14	Orth.	CaCO ₃ + 0.2 N HNO ₃	22.2	+8.7	16.0	+2.5	20.7	+7.2	2.4
14a	Alun.		23.8	+10.3	14.8	+1.3	23.0	+9.5	1.7
15	Alun.	CaCO ₃ + 0.01 N HCl + manure extract	42.2	-48.1	90.2	-0.1	142.5	+52.2	1.4
15a	Orth.		43.8	-46.5	93.6	+3.3	102.6	+12.3	1.5

16	Alun.	CaCO ₃ + 0.2 N HNO ₃ + manure extract	55.7	-34.6	119.4	+29.1	129.5	+39.2	1.5
16a	Orth.		47.5	-42.8	102.9	+12.6	115.0	+24.7	1.6
17	Mix.		48.9	-41.4	112.0	+21.7	109.3	+19.0	1.1
18	Mix.		44.1	-46.2	118.6	+28.3	119.8	+29.5	1.3
19	Orth.		44.7	-45.6	100.8	+10.5	96.4	+6.1	0.9
19a	Alun.	CaCO ₃ + 0.1 N HCl + manure extract	52.6	-37.7	88.4		117.1	+26.8	0.6
20	Alun.	CaCO ₃ + 1.0 N HNO ₃ + manure extract	54.4	-35.9	124.7	+34.4	112.6	+22.3	0.0
20a	Orth.		47.8	-42.5	126.0	+35.7	102.6	+12.3	0.0
21	Mix.	CaCO ₃ + 1.0 N HNO ₃ + 0.1 N HCl + manure extract	53.5	-36.8	137.7	+47.4	144.1	+53.8	0.4
22	Orth.		51.5	-38.8	99.4	+9.1	132.4	+42.1	6.3
23	Alun.	CaCO ₃ + 1 per cent citric acid + manure extract	57.5	-32.8	95.4	+5.1	97.4	+7.1	6.3
24	Mix.		44.6	-45.7	98.3	+8.0	144.0	+53.7	6.2
25	Orth.	Non-sterilized	13.6		11.7		16.4		8.6
26	Alun.		16.0	Check	11.9	Check	12.5	Check	6.9
27	Mix.		15.6		15.6		13.8		8.4

*K added with manure extract..... 76.8 mgm.
 Average water-soluble K added..... 13.5 mgm.
 Total K added in soluble form 90.3 mgm.

are by no means the maximum since a considerable part of the water-soluble potassium was undoubtedly held by the absorptive power of the minerals.

The pH values were determined in order to ascertain the relationship, if any, between the reaction of the solution and the liberation of potassium. From the figures obtained and from the graph in figure 2, it is evident that the reaction of the solution had no effect on the liberation of potassium.

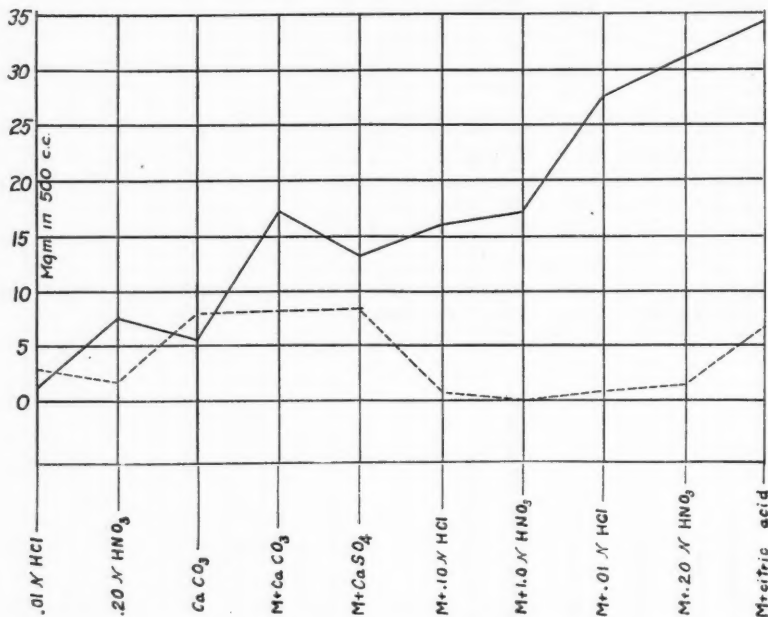


FIG. 2. GRAPH SHOWING AVERAGE INCREASE IN WATER-SOLUBLE POTASSIUM AND pH VALUES OF THE DIFFERENT TREATMENTS AFTER SIXTEEN WEEKS

———— water-soluble potassium; ----- pH value

PART II

Experiments in soil

Carrington loam secured from plot 107 of the humus plots of the Iowa Station was used as the basis of these experiments. This plot has been kept fallow since 1908 and has received no treatment whatever. A sample of the soil to a depth of eight inches was taken, air dried, and sieved. The total potassium content was 30,588 pounds per acre of 2,000,000 pounds of surface soil, and the lime requirement as determined by the Truog method was two tons. Five hundred grams of air-dry soil were thoroughly mixed with the various materials in bottles as in part 1, and distilled water was added to obtain the optimum moisture content, which was 25 per cent. For the alundum and quartz treatments, the optimum moisture was 11 per cent. With the air-dried manure and clover hay applications, it was necessary to add their equivalent weight in water in order to bring those treatments up to

the optimum moisture. During the progress of the experiments, the moisture content was maintained by regulating the moisture content of the air which was continually passed over the soil. Air drawn through a solution of 30-35 per cent H_2SO_4 contained approximately the amount of moisture required to keep the soil at the optimum.

The carbon dioxide determinations were made according to the method of Potter and Snyder (23). Since sterile air was imperative for part of the experiments, it was necessary to make a slight modification in the apparatus. An absorption tower packed with sterile cotton was placed between A and B, and also between C and D shown on figure 1, page 282 in Potter and Snyder's report. The towers filled with cotton were sterilized in the autoclave every three or four weeks in order to destroy any organisms which might enter.

The carbon dioxide was determined at intervals of one, three, five, seven days, and every seventh day thereafter. The soils were sterilized three times in the autoclave at 15 pounds pressure for three hours with intermissions of 36 hours each. This was found to be necessary to destroy all microorganisms and spores. The apparatus was of necessity sterilized in several parts which had to be reassembled before the experiment could be started. This operation naturally increased the possibilities for contamination. During the course of the experiment, several instances of such contaminations were observed but in each case the contaminated bottles were resterilized and no further difficulties were encountered.

At the end of the experiments the sterilized soils were tested for bacterial contents, and all proved to be sterile.

Series 1

This series was planned primarily to ascertain whether results obtained in part 1, could be duplicated in soils. Orthoclase was applied to the soil in portions of 20 gm. per treatment. Manure was used at the rate of 8 tons per acre and acid phosphate at the rate of 400 pounds. $CaCO_3$ and $CaSO_4$ were applied at the rate of 3 tons per acre. The lime requirement was regulated by adding a certain amount of HCl which would give approximately the required acidity conditions; then the final adjustment was determined by the Truog acidity test. The treatments are shown in table 2.

Each treatment was prepared in six duplicates, two of which were not sterilized, two were sterilized, but not kept sterile, and two were sterilized and kept sterile. The duration of the experiments was 8-11 weeks, but for convenience all calculations for total carbon dioxide are based on 10 weeks. The results of the first titrations are not included in the calculations because it was thought that the carbon dioxide obtained was largely accumulated and not formed as a result of the treatment. The results showing the total carbon dioxide production, the water-soluble potassium, and the pH values are given in table 2 and plotted in figure 3.

Although the manure extract appeared to be the most effective single factor in the experiment with potassium bearing minerals in part 1, such was not the case with manure in this test. The suggestion might be made that manure and manure extract act differently. This was determined by conducting a separate experiment to compare the effect of manure with that of manure extract. The treatments were prepared in duplicates similarly to the sterile set in series 1. Four grams of manure and 50 cc. of manure extract were used as a basis for comparison. The results secured in eight weeks are given in table 3 from which it can readily be seen that the difference, which is slightly in favor of the manure extract, is not large enough to be significant.

The application of manure in series 1 was relatively small and although there was an apparent increase in soluble potassium, its effect was not nearly so outstanding as that observed in Part 1.

It is interesting to note that the addition of orthoclase resulted in a slight increase in water-soluble potassium both when applied alone and when in com-

ination with CaSO_4 . This would indicate that the potassium in ground orthoclase is more readily attacked than the soil potassium. This statement finds support in the experiments of Magnus (17) and Hopkins and Aumer (15).

TABLE 2

Water-soluble potassium, total carbon dioxide and pH values of sterile and non-sterile soils of series 1, calculated from averages of duplicates

SAMPLE NUMBER	SOIL TREATMENT	NOT STERILIZED			STERILIZED BUT NOT KEPT STERILE			STERILIZED AND KEPT STERILE		
		K per acre	CO_2 in 500 gm. soil	Reaction	K per acre	CO_2 in 500 gm. soil	Reaction	K per acre	CO_2 in 500 gm. soil	Reaction
		lbs.	gm.	pH	lbs.	gm.	pH	lbs.	gm.	pH
1	Check	57.9	1.724	5.2	82.1	2.407	5.0	67.6	0.934	5.1
2	Orthoclase	64.4	1.920	5.3	95.0	2.473	5.1	70.8	1.183	5.2
3	Manure	69.2	2.625	5.5	91.8	2.678	5.3	96.6	1.260	5.2
	<i>Manure</i>									
4	CaCO_3 Orthoclase	72.4	2.451	6.6	128.9	2.422	5.3	93.4	0.903	6.1
5	CaCO_3 + Orthoclase + acid phos.	69.2	2.658	6.6	159.3	2.607	5.4	86.9	0.799	5.6
6	CaSO_4	99.8	2.190	5.1	179.2	2.454	5.1	112.7	0.844	5.1
7	CaSO_4 + Orthoclase	112.7	2.367	5.2	135.3	2.488	5.1	125.5	0.907	5.1
	<i>Orthoclase and HCl to adjust to lime req. of 3 tons</i>									
8	—	83.7	1.914	4.9	103.1	2.524	4.7	96.6	0.995	4.6
9	Manure	109.5	2.005	4.9	160.8	2.507	4.7	115.9	1.010	4.7
10	Manure + acid phos.	138.5	2.441	4.6	157.9	2.474	4.7	143.3	1.107	4.7
	<i>Orthoclase and HCl to adjust to lime req. of 5 tons</i>									
11	—	107.9	1.977	4.1	172.4	2.563	4.1	149.8	0.992	4.4
12	Manure	186.8	1.972	4.2	164.3	2.536	4.2	220.7	0.991	3.9

TABLE 3

Water-soluble potassium and total carbon dioxide from soil treated with manure and manure extract, calculated from averages of duplicates

TREATMENT	K PER ACRE	TOTAL CO_2 IN 500 GM. SOIL
	lbs.	gm.
Manure.....	101.4	1.453
Manure extract.....	104.7	1.493

The relatively small application of CaSO_4 resulted in a decided increase in water-soluble potassium in both sterile and non-sterile soils. Although these results support the observations of McMiller (21) and Bradley (4) it should not be overlooked that negative results might be secured if the treatment were

applied to soil types derived from orthoclase bearing rocks as suggested by Briggs and Breazeale (5). The possible cause of the beneficial effect of CaSO_4 as suggested by Bradley (4) is that the cation of the gypsum is fixed by the soil and a corresponding quantity of potassium goes into solution to form K_2SO_4 . The conclusion reached by Dussere (9) who claimed that the liberation of potassium from soils through the applications of gypsum, ammonium sulfate, and calcium superphosphate was due to the acidity resulting from those fertilizers does not find much support in the results obtained in these experiments, since the pH value was practically unchanged by the CaSO_4 treatments. Bradley's suggestion seems more plausible, although no actual proof can be given here.

Probably the most outstanding data in this experiment are those showing the action of the acids on the liberation of potassium. It will be recalled from part 1, that the direct action of acids had no effect on the potassium bearing minerals, but when applied in combination with manure extract they produced decided effects upon the solubility of potassium. This soil contains considerable organic matter and hence an effect similar to that observed in part 1 could easily be produced. Again, the theory of Ames and Boltz (2) and of Ames (1), as to the action of salts of acids may be considered to be supported by the results of this experiment, but in this theory, the effects of colloids in the soil have been overlooked.

The striking coincidence that the increase in water-soluble potassium was invariably associated with a corresponding increase in hydrogen-ion concentration leads to another possibility suggested by the work of Gordon and Starkey (13). They showed that a small change in hydrogen-ion concentration around pH 7 was followed by a large decrease in the absorption of potassium by silica gel and that when the hydrogen-ion concentration was further increased the potassium became correspondingly less absorbed and consequently more available. Their results seem to be in agreement with those reported in tables 1 and 2, with the exception of the treatments which have a hydrogen-ion concentration of less than pH 1.0.

If pure, artificial silica gels manifest a lesser absorptive capacity for potassium under acid conditions, it is not unlikely that the silica colloids and gels in the soil exhibit a similar behavior. Silica colloids and gels according to Ostwald (22) constitute one of the four most important classes of soil colloids. Consequently they were very likely present both in the soil and in the minerals used in these experiments. Furthermore, they were probably present in the soil which McCall and Smith, Ames and Boltz, and Ames used. Although those investigators did not determine the hydrogen-ion concentration, they found an appreciable increase of water-soluble potassium only under acid conditions. These striking coincidences would certainly lead to the suggestion that possibly the condition of the colloidal material in general and of silica gels in particular are to a large extent responsible for the amount of potassium obtained in water extracts.

The results in table 2, obtained in sterilized soil subsequently exposed to non-sterile air, show the highest amounts of water-soluble potassium and carbon dioxide. Sterilization was undoubtedly responsible for part of the increase in water-soluble potassium but it will be noticed that the soil which was kept sterile throughout the experiment gave lower results in all treatments except in no. 18. No explanation can be offered for this exception.

The difference then between the sterilized soil which was exposed to non-sterile air and that which was kept sterile must be due to some factor other than sterilization. The carbon dioxide production of the former was about three times greater than that of the latter, and considerably greater than that of the unsterilized soil. This large carbon dioxide production was probably due to the action of molds which formed an exceptionally dense growth on all the sterilized soils subsequently exposed to non-sterile air. It seems that in the absence of competing organisms those molds were very active in the decomposition of organic matter, with the result that decidedly increased amounts of carbon dioxide and slightly increased amounts of water-soluble potassium were produced. The relation of carbon dioxide production to the liberation of potassium will be considered in series 2.

Series 2

The purpose of this series was to determine the effect of relatively large amounts of organic matter on the liberation of soil potassium. Soil and orthoclase were used in the same manner as in series 1. Since the absorptive power of soil offers the chief difficulty in water-soluble potassium determinations, alundum, which is a non-absorbent and inert material, was introduced into the series in order to give an estimate of the amount of water-soluble potassium absorbed by the soil during the course of the experiment. Quartz, although absorbing a small amount of potassium, was used in comparison with alundum. CaCO_3 and acid phosphate were applied to study their effect when combined with large amounts of organic matter. CaCO_3 was used at the rate of four tons per acre and acid phosphate at the rate of 1000 pounds per acre. When alundum and quartz were used the potassium applied consisted in a mixture of 50 gm. of orthoclase and 50 gm. of alunite.

Manure was added at the rate of 16 and 32 tons per acre and clover hay at the rate of 4 and 12 tons per acre. The manure contained 1.071 per cent or 21.42 pounds of total potassium per ton, and the clover hay 0.981 per cent or 19.62 pounds per ton. As a large part of this potassium is in a soluble form, the total amount was deducted from the final results in table 5.

During the second week of the experiment a leak in the apparatus of the sterile set, caused contamination of all the bottles with the exception of sample 19-a. The contaminated bottles were resterilized, but separate analyses were made of the one that was not contaminated. The arrangement of the test is shown in table 4.

Each treatment was prepared in quadruplicate, two kept sterile and two non-sterile. The duration of the experiment was 11 weeks for the sterile and 12 weeks for the non-sterile. For convenience, the total carbon dioxide was calculated on the basis of 10 weeks. The results of the water-soluble potassium, the total carbon dioxide and the pH values are reported in table 4. The amount of water-soluble potassium added in the form of manure and orthoclase is not taken into account. According to Fraps (11) the water extract from the soil does not necessarily represent the solubility of the potassium minerals exposed to the action of the solvent, but the difference between the potassium dissolved by the solvent and the soluble potassium absorbed by the soil. This absorbed potassium of the soil is

TABLE 4

Water-soluble potassium, total carbon dioxide, and pH value from sterile and non-sterile soils of series 2, calculated from averages of duplicates

SAMPLE NUMBER	TREATMENT				NOT STERILIZED				STERILIZED AND KEPT STERILE		
	Manure	CaCO ₃	Acid phosphate	Clover hay	K per acre	Citrate soluble K per acre	CO ₂ in 500 gm. soil	Reaction	K per acre	CO ₂ in 500 gm. soil	Reaction
	gm.	gm.	gm.	gm.	lbs.	lbs.	gm.	pH	lbs.	gm.	pH
13	8	2			125.5	505.2	3.207	6.8	188.2	2.710	4.8
14	16	2			164.1	553.4	3.435	7.0	271.9	2.665	6.0
15	16	2	0.25		202.9	460.1	3.350	6.8	328.2	2.854	5.6
16	16				199.7	637.1	3.297	6.1	352.3	2.877	4.9
17				2	80.5	405.4	2.714	4.9	143.2	2.469	4.6
18				6	167.5	421.5	3.231	4.8	189.8	2.774	4.4
19		2		6	165.9	341.1	3.140	6.3	204.3	2.146	5.6
19a									151.2	1.661	
20		2	0.25	6	180.4	370.0	3.085	6.3	165.7	2.075	5.3
21	8*				325.0	431.2	2.162	8.9	350.7	1.835	7.9
22	8*	2			327.0	617.8	2.331	9.1	331.4	1.991	9.1
23	8†				304.1		2.423	8.2	297.6	1.772	7.3

* Alundum added.

† Quartz added.

TABLE 5

Increase or decrease in water-soluble potassium due to treatment, after deduction of soluble amounts added in the form of organic matter and orthoclase

SAMPLE NUMBER	TREATMENT				NOT STERILIZED					STERILIZED AND KEPT STERILE				
	Manure	CaCO ₃	Acid phosphate	Clover hay	K per acre	K added	Decrease	K second extract	Increase or decrease	K per acre	K added	Increase or decrease	K second extract	Increase
	gm.	gm.	gm.	gm.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
13	8	2			125.5	352.5	-127.0			188.2	352.5	-164.3		
14	16	2			164.1	697.2	-533.1			271.9	697.2	-426.3		
15	16	2	0.25		202.9	697.2	-494.3			328.2	697.2	-369.0		
16	16				199.7	697.2	-497.5	115.8	-381.7	352.3	697.2	-344.9		
17					80.5	89.2	-8.7			143.2	89.2	+54.0		
18				6	167.5	246.2	-78.7			189.8	246.2	-56.4		
19		2		6	165.9	246.2	-80.3			204.3	246.2	-41.9		
20		2	0.25	6	180.4	246.2	-65.8			165.7	246.2	-80.5		
21	8*				325.0	396.7	-71.7	80.4	+8.7	350.7	396.7	-46.0	98.1	+52.1
22	8*	2			327.0	396.7	-69.0	78.8	+9.0	331.4	396.7	-65.3	99.7	+34.4
23	8†				304.1	396.7	-92.6			297.6	396.7	-99.1		

* Alundum added.

† Quartz added.

only very slowly acted upon by water. Vanatta (27) found that boiling twice for a period of two hours failed to release any considerable amounts of absorbed potassium.

It was found necessary in series 2 to make a second water extract on the two sterile and non-sterile alundum samples, in order to remove the potassium held mechanically. A second extract was also made of one of the treated soils. The results of this second analysis, together with the increase or the decrease of water-soluble potassium after deduction of that added in the form of minerals and manure are reported in table 5. The water-soluble potassium of the minerals was taken from the average amount found in part 1.

The results in table 4 show an apparent increase in water-soluble potassium corresponding roughly to the increase in organic matter added. However, when the soluble potassium added in the form of manure, clover hay and orthoclase was subtracted as shown in table 5, there was a decrease in water soluble potassium throughout the series. This decrease was undoubtedly due to the absorptive power of the soil.

According to Anderson (3) and his associates, 95 per cent of the absorption of potassium in soils is due to colloidal material. This absorbed potassium is only very slowly given up by the action of water. McCall, Hilderbrandt and Johnston (18) found that the curve showing the amounts of potassium removed by successive washings of a soil through which a solution of KCl had been percolated was almost a straight line. It is also possible that some of the soluble potassium was held in loose combination with small mineral particles. That would probably account for the relatively large amounts of potassium obtained in the second extract, notably the extract of sample 16. It would be noted that the sum of the two extracts of the sterile and non-sterile alundum treatments given in table 5, do not necessarily represent the total potassium that was rendered soluble in the experiment. The minerals and the manure very likely contained materials which formed colloidal complexes capable of absorbing potassium. Hence, in view of the fact that the absorption factor was not considered, and that, only 95.1 per cent of the potassium in the manure was water-soluble, the increases due to the action of manure indicated in table 5, are probably too low.

It is of interest to note that the positive results with the liquid medium in part 1 were almost duplicated with the alundum medium but that the soil itself gave negative results.

The official method with neutral ammonium citrate was used on the unsterilized treatments of series 2, in an attempt to ascertain the amount of absorbed potassium. The results are reported in column 3 of table 4, and since they show no indication of the quantities of absorbed potassium in those soils the method was discontinued.

The result reported in table 5, for the second extract of sample 16, might lead to the belief that repeated water extractions would give satisfactory results, but it should not be overlooked that the amount reported was far from the total amount absorbed. Furthermore, at least part of the potassium in the extract was probably held loosely around small particles instead of in the absorbed form. Schreiner and Failyer (24) passed a solution of KCl through various

soils and by continuous percolation of water, obtained amounts of potassium which showed no indications of the quantity absorbed by the soil. The more recent work of McCall (18) and his associates showed that only very small amounts of absorbed potassium were given up in repeated water extractions.

All this goes to show that the chief difficulty in the determination of soluble soil potassium lies unquestionably in the absorptive power of the soil colloids and that other methods differing from the water extract method should be resorted to.

The addition of calcium carbonate and acid phosphate showed no appreciable effect on the liberation of potassium and the production of carbon dioxide. The slight differences reported in table 4 are easily within the limits of experimental error.

The application of organic matter in the form of manure and clover hay increased the carbon dioxide production in the soil. Comparatively small applications of clover hay appeared to have a decided effect on the carbon dioxide production. The maximum production for the Carrington loam seemed to be reached with applications of 16 tons of manure per acre. Larger applications did not increase the carbon dioxide production to any extent. More carbon dioxide was produced in the soil than in quartz, due to the decomposition of the organic matter in the soil. There seemed to be a close relationship between the carbon dioxide production and the liberation of potassium as indicated by the water-soluble method. The curves in figure 3, show that this relationship holds for the soils, but not for the alundum and quartz due probably largely to the absorption factor.

The sterilization of soils would naturally be expected to result in a decided decrease in carbon dioxide production since all bacterial action is stopped. The investigations of Deherain and Demoussy (7) Wollny (28) and Severin (25) indicated that comparatively little carbon dioxide was produced in sterile soils and that the ratio between the amounts produced in sterile and non-sterile soils was 1:10.

The results of this experiment as reported in table 4 showed that considerable carbon dioxide was produced in the sterile soils. In fact, the quantities produced amounted to approximately 50 per cent of that in the non-sterile duplicates of series 1 and approximately 70-75 per cent of the non-sterile duplicates of series 2. The reason for the higher results in series 2, is found in the fact that all the bottles except one were resterilized. Heat and pressure in the autoclave seemed to have an effect on the production of carbon dioxide as well as on the soluble potassium of soils. The results in table 6, show that sample 19 produced approximately 24 per cent more carbon dioxide than its duplicate which did not get contaminated. Therefore, if 24 per cent of the carbon dioxide were subtracted from the results of the sterile part in series 2, the curves in figure 3 would show approximately the same relationship in both series. It seems that those corrected results would represent largely amounts of carbon dioxide produced by purely chemical action.

The contention of Stoklasa and Ernest (26) that the two sources of carbon dioxide in soil are bacterial activities and plant root action does not find much support in the results of these experiments, because neither bacteria nor plant roots were present. It is true that the effect of sterilization may have started the breaking down of the organic matter so that hydrolysis and catalytic action could be more effective. However, the production of carbon dioxide in the sterile soils occurred similarly to that in non-sterile soil; the first four or five weekly determinations gave the largest quantities and thereafter a gradual decrease was noticeable.

TABLE 6

Total water-soluble potassium and carbon dioxide of sample 19 sterilized two times and of its duplicate sterilized once

SAMPLE NUMBER	K PER ACRE	CO ₂ IN 500 GM. SOIL
	lbs.	gm.
19 sterilized twice.....	204.3	2.146
19-a sterilized once.....	151.2	1.661

TABLE 7

*Water-soluble potassium per acre and freezing point depression of soils sterilized once, compared with those sterilized twice**

TREATMENT	STERILIZATION	TOTAL WATER-SOLUBLE POTASSIUM	FREEZING POINT DEPRESSION	INCREASE
		lbs.	°C	per cent
Sterilized twice, 16 T.M.† applied	Non-sterile	170.5		
	Sterile	233.3		36.7
Check sterilized once	Non-sterile	56.3		
	Sterile	70.8		25.7
Optimum moisture, sterilized twice, 16 T.M. applied	Non-sterile		0.252	
	Sterile		0.708	25.5
Soil extract, sterilized once, 16 T.M. applied	Non-sterile		0.027	
	Sterile		0.036	25.0

* Sterilization was done as described in the experimental procedure of part 2.

† T.M.—Tons of manure.

The water-soluble potassium was increased invariably in all sterilized treatments, yet the carbon dioxide production was decreased 50 per cent or more. The results show that there was absolutely no relation between the carbon dioxide production and the liberation of potassium in the soil and that the sterilization caused large amounts of potassium to become water-soluble.

Lyon and Bizzell (16) found that sterilized soil yielded decidedly more soluble potassium and other plant food. The results in table 7, show some interesting relations between the soluble potassium and the total salts in solu-

tion in the sterile and non-sterile soils. One sterilization resulted in an increase of 25.7 per cent in water-soluble potassium, and 25.0 per cent in the freezing point depression of the soil solution. Two sterilizations caused an increase of 36.7 per cent in the water-soluble potassium and 25.5 per cent in the freezing point depression of the soil solution. It appears, therefore,

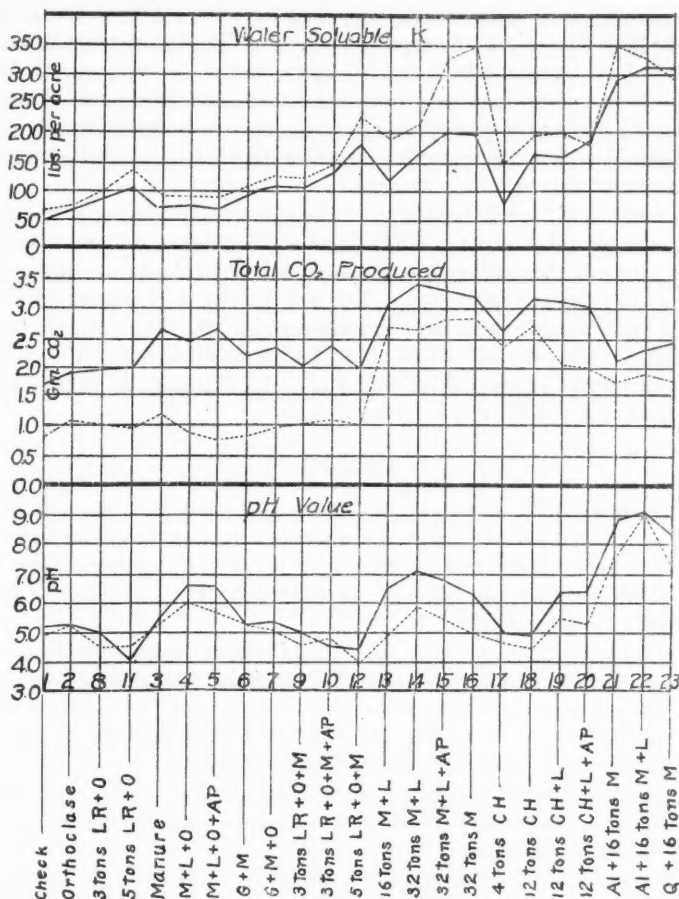


FIG. 3. GRAPH SHOWING THE RELATION BETWEEN THE PRODUCTION OF CARBON DIOXIDE AND THE LIBERATION OF WATER-SOLUBLE POTASSIUM IN STERILE AND NON-STERILE SOILS, AND THE RELATION OF THE pH VALUE TO THE PRODUCTION OF CARBON DIOXIDE, OR THE LIBERATION OF WATER-SOLUBLE POTASSIUM IN THE SAME SOILS

— non-sterile; - - - sterile; M, manure; L, CaCO₃; G, CaSO₄; CH, clover hay; O, orthoclase; Al, alunite; Q, quartz; AP, acid phosphate; LR, lime requirement.

that heat and pressure have a decided effect on the solubility of potassium and other plant foods.

Comber (6) found that heat caused the dehydration and breaking up of colloidal aggregates which exposed a larger surface to the solvent agencies and resulted in a larger quantity of soluble material. It is reasonable to suppose that heat and pressure in sterilization have a similar effect and, consequently, the higher yields of water soluble potassium from the sterilized soils shown graphically in figure 3 are only apparent. A correction of 25 per cent for series 1, and 36.7 per cent for series 2, should be made before the results can be compared. Such a correction would show that the amount of water-soluble potassium in the sterile soils was approximately the same as in the non-sterile soils. It appears then that the production of carbon dioxide has no direct relation to the amount of water-soluble potassium.

The reaction of the soils seemed to be affected to a slight degree by sterilization. The pH values given in tables 2 and 4 indicate that for some unknown reason nearly all the sterilized soils gave a slightly higher hydrogen-ion concentration than the non-sterile soils. The soil reaction as a whole, however, proved to be of minor importance in these experiments. The curves in figure 3, which represent the pH values of all the treatments in part 2, show absolutely no relation between these values and the liberation of water-soluble potassium or the production of carbon dioxide.

SUMMARY

These tests permit of certain conclusions. The fact that the absorptive power of colloidal matter prevented the complete removal of all the liberated potassium by water extracts indicates that the amounts recovered with the water-soluble method are not as large as they should be but they are satisfactory for comparative purposes.

1. A manure extract and a combination of manure extract and acids in moderate concentrations gave a decided increase in water-soluble potassium from finely ground orthoclase and alunite in water solutions. Sterilization and the addition of acids, calcium carbonate, and calcium sulfate did not increase the water-soluble potassium of the same minerals.

2. The application of relatively small amounts of calcium sulfate to Carrington loam caused an increase in water-soluble potassium while calcium carbonate and acid phosphate did not.

3. The action of contaminating forms, consisting largely of molds, resulted in a decided increase in carbon dioxide and a smaller increase in water-soluble potassium in sterilized soil.

4. Organic matter such as manure and clover hay, and a combination of acids and organic matter applied to sterile and non-sterile soil resulted in an increase of water-soluble potassium. This increase, due to the absorptive power of the soil colloids, was less than the amount of soluble potassium applied in the form of manure and clover hay.

5. The production of carbon dioxide did not prove to be an index of the quantity of water-soluble potassium liberated. The maximum carbon dioxide production was secured with applications equivalent to 16 tons of manure per acre.

6. The carbon dioxide produced in sterile soils was approximately 50 per cent of that obtained in the non-sterile duplicates.

7. Sterilization resulted in a decided increase in the concentration of the soil solution and in the amount of water-soluble soil potassium. It also resulted in a slight increase in the hydrogen-ion concentration of the soil.

8. The reaction of the soil showed no relation to the carbon dioxide production or to the liberation of potassium, but there seemed to be some indication that a hydrogen-ion concentration less than pH. 6 decreased the potassium-absorbing power of soil colloids.

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THE LEACHING OF ALKALI SOIL

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The following methods have been used with varying degrees of success for reclaiming alkali soil or for alleviating temporarily its ill effects: (a) plowing the surface soil and maintaining the alkali at a low level by systematic use of irrigation water; (b) quickly flooding the soil and then draining it; (c) removing the alkali from the surface by scraping; (d) growing alkali-tolerant crops; (e) neutralizing the alkali by chemicals or organic matter. These methods have been practiced with varying degrees of success. But in the majority of cases where the alkali has accumulated in quantities sufficient to materially interfere with plant growth they can be considered as mere temporary expedients. The only permanent procedure is the installation of underground drains. In some soils and with specific salts this is highly successful, whereas with other soils or with different salts it is either only a partial success or a total failure. The failure is often due to the imperviousness of the soil to water which makes leaching impossible. At times the soil is readily leached of its alkali content but is barren for a number of years after the leaching.

This work was undertaken to determine the rapidity with which the various salts leach from different soils, the quantity of plant-food which is taken from the soil in the leaching, and the chemical and biological changes which have resulted from the action of the various salts upon the soil and their removal. In this paper we shall deal with the chemical phase of the subject and in a subsequent article the biological phase will be considered.

PLAN OF EXPERIMENT

Two-gallon jars, provided with a half-inch hole near the lower edge were used. Into these holes were fitted rubber stoppers and glass tubes so that all drainage water could be collected, measured, and analyzed. A small quantity of glass wool was placed over the opening and the bottom of the jar was covered to a depth of two inches with fine gravel. This was covered with a layer of glass wool. Sufficient soil to fill the pots was mixed with the requisite salts, packed into the pots, and the moisture content made to 20 per cent. Some pots contained untreated, natural alkali soils. The salts treatments were as follows:

- 2 per cent sodium chloride
- 2 per cent sodium sulfate
- 2 per cent sodium carbonate
- 1 per cent sodium chloride plus 1 per cent sodium sulfate
- 1 per cent sodium chloride plus 1 per cent sodium carbonate
- 1 per cent sodium sulfate plus 1 per cent sodium carbonate
- $\frac{2}{3}$ per cent each sodium chloride, sodium sulfate, and sodium carbonate

In one of the natural alkali soils the chlorides predominated, in another the sulfates, and in still another the carbonates. Eight pots were used for each treatment, six of which were leached and the other two unleached; results are reported as averages of six or two pots, respectively. Both the natural and artificial alkali soils were permitted to stand for two months with a moisture content of 20 per cent before leaching so that the reactions which were going to occur would tend toward equilibrium. At the close of this period six pots in each series were leached. This was done by keeping a "water head" on them as near constant as possible. All drain water was collected and the following data taken:

Time necessary to leach each specific salt from the soil

Quantity of water required for the leaching

Analysis of approximately every 2000 cc. of the drainage water for the specific salts added and for phosphorus, potassium, nitrogen, and carbon.

COMPOSITION OF SOIL USED

The work was conducted on four different soils:

1. From the College Farm just east of the Plant Industry Building
2. From Corinne
3. From Benson Ward
4. From Richland Acres

Soil 1 was a good productive soil and was made unproductive by the addition of the salts listed above. Soils 2, 3 and 4 were natural alkali soils containing sufficient alkali to prevent the growth of all vegetation except a few salt-tolerant plants. The physical analyses of the four soils as determined by the Yoder (16) elutriator are given in table 1.

TABLE 1
Physical composition of soils

CONSTITUENTS	COLLEGE FARM SOIL	CORINNE SOIL	BENSON WARD SOIL	RICHLAND ACRES SOIL
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Sand.....	36.6	17.5	42.5	4.8
Fine sand.....	30.6	17.3	20.9	29.6
Coarse silt.....	18.8	28.5	19.0	27.0
Medium silt.....	6.0	15.9	3.8	13.1
Fine silt.....	2.3	5.3	2.3	10.2
Clay.....	3.5	7.4	6.1	9.4
Moisture, soluble salts, and loss.....	2.2	8.1	5.4	5.9

Soils 1 and 3 are sandy loams whereas soils 2 and 4 are fine sandy loams. These soils should be more difficult to leach than a sand and much less difficult than a tight or heavy clay. However, they represent approximately the composition of the average alkali soil. Therefore the results obtained in this work should give a fair idea of what may be expected in the field with the various alkali soils.

RATE OF PERCOLATION

The results reported in table 2 are averages for the six pots leached. The containers in which the drain waters were collected held approximately 2500 cc. and it was planned to empty, measure, and note the time when the bottles were about two-thirds full. Leaching was continued until an analysis of the drain water indicated that the greater portion of the soluble salts had been leached from the soil.

The water passed rather rapidly through the untreated soil. The first 48 hours yielded an average hourly leaching of 29.4 cc.; during the second period this dropped to 23.6 cc. and then showed a rise. It is quite evident that there is no great increase or decrease in speed of leaching during a period of eighteen days. Probably had this been continued longer there may have been a decrease since the soil tended to compact. The average amount of water leached through the untreated soil was 29.5 cc. per hour. This soil treated with 2 per cent sodium chloride leached at about the same rate at first, but during the second period the leaching dropped to 8.2 cc. per hour and never again throughout the experiment exceeded 11.3 cc. per hour. Therefore the average drainage from the soil treated with sodium chloride was only 11.7 cc. per hour, which is about 40 per cent of that passing through the untreated soil in unit time.

TABLE 2
Rate of percolation in soil treated with various sodium salts

NO TREATMENT		2 PER CENT NaCl		2 PER CENT Na ₂ CO ₃		2 PER CENT Na ₂ SO ₄	
Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour
<i>hours</i>	<i>cc.</i>	<i>hours</i>	<i>cc.</i>	<i>hours</i>	<i>cc.</i>	<i>hours</i>	<i>cc.</i>
48	29.4	60	26.3	142	8.5	56	36.7
71	23.6	279	8.2	374	5.2	57	32.3
52	36.8	274	8.1	506	3.7	60	30.9
56	36.8	223	11.3	594	2.9	76	28.4
66	28.1	222	8.9	711	2.3	85	22.5
72	25.4	127	7.9	800	1.9	115	17.7
71	26.5			928	1.8	91	19.2
				1096	1.4	83	22.4
				1417	1.1	44	55.2
						29.5	63.9

Soil treated with 2 per cent of sodium carbonate leached very slowly even at first, and by the end of one year only 1 cc. per hour was passing through the soil. The average drainage from this soil was only 3.2 cc. per hour, which is only about 11 per cent of normal as compared with the untreated soil. *The soil and drainage water became dark in color.* It puddled greatly and shrank in volume so that it did not fill the containers. Apparently, the granular structure had been broken down completely (fig. 1).

Soil treated with 2 per cent sodium sulfate leached more rapidly than did the untreated soil. For a short time during the middle of the leaching period this soil for some unknown cause leached more slowly than the untreated soil. However, the average for the entire time was 32.9 cc. per hour which is 112 per cent as compared with the untreated soil. This is due to the flocculating effect of the sodium sulfate upon the soil. It is likely that much of the benefit which has been found (11, 12) to result from the use of sulfates upon this soil is due in a measure to flocculation which increases the aeration of the soil and correspondingly the activity of the aerobic bacteria of the soil.

The average results for the mixture of two sodium salts as compared with the untreated soil are given in table 3.

A soil in which there is a mixture of sodium chloride and sodium sulfate leaches nearly as readily as a soil containing only sodium sulfate. But neither sodium chloride nor sodium sulfate increases the permeability of black alkali soil for water. The soil receiving the mixture of sodium chloride and sodium carbonate leached a little more rapidly at first than soil containing only sodium carbonate. But such soil soon became as impervious to water as soil containing only sodium carbonate. The soil containing the mixture of carbonate and sulfate was in very bad physical condition from the first and leached very slowly. It was impossible to get enough water through the soil to leach out sufficient salt to permit plants to grow.

TABLE 3
Rate of percolation in soil treated with combinations of sodium salts

NO TREATMENT		1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄		1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃		1 PER CENT Na ₂ CO ₃ + 1 PER CENT Na ₂ SO ₄	
Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour
<i>hours</i>	<i>cc.</i>	<i>hours</i>	<i>cc.</i>	<i>hours</i>	<i>cc.</i>	<i>hours</i>	<i>cc.</i>
48	29.4	48	29.2	141	14.7	154	5.5
71	23.6	52	40.6	527	3.2	84	2.2
52	36.8	68	28.3	665	2.1	1135	1.4
56	36.8	45	34.3	812	1.9	966	1.5
56	28.1	87	20.7	1883	1.0	1353	1.3
72	25.4	147	13.7	1328	1.3	1177	1.3
71	26.5	54	34.1				
		48	33.7				
		48	39.9				

The results obtained on leaching a synthetic alkali soil containing a mixture of sodium chloride, sodium sulfate, and sodium carbonate and natural alkali soils are given in table 4. The synthetic soil contained 2 per cent of alkali, one-third of which was chloride, one-third sulfate, and the remaining one-third carbonate. In the Corinne soil the chlorides predominated, in the Richland Acres soil the sulfates, and in the Benson Ward soil, the carbonates.

The prepared soil containing the mixture of chlorides, sulfates, and carbonates leached more slowly than soil containing either chlorides or sulfates, but much more rapidly than soils containing only sodium carbonate.

The natural alkali soils, with the exception of the Corinne soil, leached more rapidly than the prepared soil. The slow leaching of the Corinne soil was due not alone to its alkali content but to the fine texture of the particles composing it. Both the synthetic alkali soil and the Benson Ward soil held very tenaciously to the salts and neither was sufficiently reduced in alkali content to permit the germination of plants even after leaching for 207 and 138 days, respectively. As the salts were removed from the prepared alkali soil the

water passed through more rapidly, but all were in an extremely bad state of tilth after leaching. It is evident from these results that the speed with which water passes through an alkali soil is dependent upon the specific alkalies present and the texture of the soil. This is clearly brought out in table 5

TABLE 4
Rate of percolation in soil treated with chlorides, carbonates and sulfates

NO TREATMENT		NaCl + Na ₂ SO ₄ + Na ₂ CO ₃		CORINNE SOIL		RICHLAND ACRES SOIL		BENSON WARD SOIL	
Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour
hours	cc.	hours	cc.	hours	cc.	hours	cc.	hours	cc.
48	29.4	161	6.6	686	2.6	64	23.5	149	9.0
71	23.6	337	6.1	914	1.9	118	15.2	232	8.0
52	36.8	362	5.5	841	1.8	193	12.2	260	6.9
56	36.8	341	5.6	1212	1.8	216	9.1	192	9.5
66	28.1	416	4.8	1412	1.2	174	7.7	182	11.0
72	25.4	477	4.2			145	8.8	191	10.0
71	26.5	590	4.4					185	10.0
		360	4.7					180	10.9
		277	7.7					189	9.4
		222	7.6					311	7.2
		207	8.9					256	7.4
		212	7.2					271	7.0
		282	8.5					253	7.6
		252	8.5					254	7.2
		270	9.3					223	10.9

TABLE 5
Relative quantities of water passing through each of the various soils in unit time

SOIL	TREATMENT	WATER LEACHED	SOIL	TREATMENT	WATER LEACHED
College	None	100	College	None	100
College	2% Na ₂ SO ₄	112	College	0.66% each NaCl + Na ₂ SO ₄ + Na ₂ CO ₃	23
College	1% NaCl + 1% Na ₂ SO ₄	103			
Richland Acres		43			
College	2% NaCl	40	College	1% NaCl + 1% Na ₂ CO ₃	14
Benson Ward		30	College	2% Na ₂ CO ₃	11
			College	1% Na ₂ SO ₄ + 1% Na ₂ CO ₃	7
			Corinne		6

which gives the relative quantities of water leached through the soil on the basis of the amount leached through the untreated soil taken as 100.

Sodium sulfate increased the rate of leaching 12 per cent, whereas the mixture of sodium chloride and sodium sulfate increased it 3 per cent. All of the other

treatments greatly decreased the leaching. This was greatest where the carbonate was used and it is evident that the presence of the other salts had little effect in overcoming the puddling effect of the carbonate.

The soils were all leached until an analysis of the drain waters indicated that the greater quantity of the soluble salt which could be removed by water had been carried from the soil. The time required and quantity of water necessary to accomplish this varied greatly with the different soils, as may be seen from table 6.

The time and the quantity of water necessary to remove the salt is a function of the kind of salt in the soil and the texture of the soil. A small volume of water in a short time removed the greater part of the chlorides and sulfates from the soil, but it required a long time to remove the carbonates.

TABLE 6
Leaching necessary to remove the greater portion of the soluble salt from the soil

SOIL	TREATMENT	LENGTH OF PERIOD		WATER LEACHED	SOIL	TREATMENT	LENGTH OF PERIOD		WATER LEACHED
		days	liters				days	liters	
College	None	18	121		College	None	18	121	
College	2% NaCl	49	84		College	1% Na ₂ SO ₄ + 1% Na ₂ CO ₃	203	85	
College	2% Na ₂ CO ₃	274	140						
College	2% Na ₂ SO ₄	29	175		College	0.66% each NaCl + Na ₂ SO ₄ + Na ₂ CO ₃	199	240	
College	1% NaCl + 1% Na ₂ SO ₄	25	153						
College	1% NaCl + 1% Na ₂ CO ₃	640			Corinne		211	79	
					Richland Acres		38	94	
					Benson Ward		139	247	

RATE OF REMOVAL OF SOLUBLE SALTS

The salts added were determined in each of the fractions of leach water collected. The average results for the sodium salts are given in table 7.

Sodium chloride was rapidly leached from the soil. There was removed in the second period 41 per cent as much salt as during the first period. The quantity per cubic centimeter was, however, 47 per cent greater during the second period than during the first. This undoubtedly occurred because the soil held the water longer, which permitted it to become more nearly saturated with salt before it drained from the soil. The yield in the third was only 2 per cent per hour of that of the first and by the fourth period it had been reduced to a fraction of 1 per cent. The quantity of salt per cubic centimeter by the fourth period had been reduced to 0.2 mgm. per cubic centimeter which indicated that most of the salt soluble in water had been leached from the soil.

Less sodium carbonate was leached from the soil per hour during the first period than sodium chloride. The quantity per cubic centimeter, however,

was much greater. By the fifth period the quantity being removed had become nearly constant, with each cubic centimeter of water carrying 2 mgm. of sodium carbonate. It would appear that uncombined or unadsorbed sodium carbonate is readily removed by water, but the combined or adsorbed salt is removed with great difficulty.

Sodium sulfate was leached from the soil even more readily than sodium chloride. These results would indicate that no trouble should be experienced in leaching sodium chloride or sulfate from a soil such as this. This should not, however, be taken as the case with all soils, for the texture of this soil was fairly coarse and it was well supplied with calcium and magnesium carbonate (5). There was no indication from the texture or color of the soil or analysis of the drainage water that the sodium chloride was being transformed into the carbonate. The removal of sodium carbonate from this soil presents considerable difficulty, for even after it had been leached for 274 days and

TABLE 7

Rate of removal of NaCl, Na₂CO₃ and Na₂SO₄ from soil containing 2 per cent of these same salts

NaCl REMOVED			Na ₂ CO ₃ REMOVED			Na ₂ SO ₄ REMOVED		
Period	Per hour	Per cubic centimeter	Period	Per hour	Per cubic centimeter	Period	Per hour	Per cubic centimeter
hours	mgm.	mgm.	hours	mgm.	mgm.	hours	mgm.	mgm.
60	712.0	27.1	142	438.1	51.5	56	1471.0	40.1
279	291.3	24.2	374	98.5	18.9	57	787.5	24.4
274	12.0	1.4	506	18.2	4.9	60	339.9	11.0
223	0.1	0.08	594	7.3	2.5	76	100.4	3.5
			711	4.7	2.0	85	37.4	1.7
			800	2.8	1.5	115	9.2	0.5
			928	2.6	1.4	91	3.1	0.2
			1096	2.2	1.6	83	1.5	0.07

140 liters of water had passed through it the soil contained sufficient black alkali to prevent the growth of plants. In addition to the large quantities of sodium carbonate present several other factors were not ideal for plant growth after leaching as will be pointed out in this and later papers.

It is evident from table 8 that in a mixture of sodium chloride and sodium sulfate the chloride leaches from the soil more readily than the sulfate. By the end of 168 hours the drainage water was nearly free from sodium chloride but was carrying appreciable quantities of sodium sulfate at the end of 501 hours of leaching. The sulfate is adsorbed more firmly by the soil in mixtures and as individual salts than the chloride. Soil containing sodium chloride and sodium carbonate yields its chloride readily but the carbonate is tenaciously held. Even after being leached for 640 days soil still yielded considerable sodium carbonate. Moreover, it is evident from these results that sodium carbonate retards the leaching of sodium chloride from the soil. This is also true for sodium sulfate. However, it does appear that the carbonate

leaches out more readily in the presence of sodium sulfate than in the presence of sodium chloride, which is due to the flocculating action of the sulfate.

TABLE 8

Rate of removal of sodium salts from soil containing combinations of the following salts

1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄			1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃			1 PER CENT Na ₂ CO ₃ + 1 PER CENT Na ₂ SO ₄		
Period	NaCl removed per hour	Na ₂ SO ₄ removed per hour	Period	NaCl removed per hour	Na ₂ CO ₃ removed per hour	Period	Na ₂ CO ₃ removed per hour	Na ₂ SO ₄ removed per hour
hours	mgm.	mgm.	hours	mgm.	mgm.	hours	mgm.	mgm.
48	940.2	478.7	141	454.6	14.0	154	14.1	293.4
52	746.1	637.1	527	39.9	11.8	843	8.8	41.4
68	26.1	321.1	665	2.3	10.3	1135	5.5	2.0
45	1.0	130.3	812		5.3	966	4.5	0.08
87		16.2	1883		2.0			
147		2.1	1328					
54		4.5						
48		3.5						

TABLE 9

Rate of removal of sodium salts from synthetic and natural alkali soils

SYNTHETIC ALKALI SOIL				CORINNE SOIL			RICHLAND ACRES SOIL			BENSON WARD SOIL			
Period	Removed per hour			Period	Removed per hour		Period	Removed per hour		Period	Removed per hour		
	NaCl	Na ₂ SO ₄	Na ₂ CO ₃		NaCl	Na ₂ SO ₄		NaCl	Na ₂ SO ₄		NaCl	Na ₂ CO ₃	Na ₂ SO ₄
hours	mgm.	mgm.	mgm.	hours	mgm.	mgm.	hours	mgm.	mgm.	hours	mgm.	mgm.	mgm.
161	272.4	265.0	5.4	658	502.8	8.1	64	163.4	727.3	149	605.1	386.6	244.3
337	30.5	44.8	13.8	914	34.3	0.8	118	18.7	168.0	232	24.7	73.2	11.4
362	1.4	1.3	10.6	841	2.4	0.05	193		4.9	260	3.8	30.6	3.0
341	0.1	0.4	9.2	1212	0.5		216		0.9	192	0.9	20.0	1.7
416		0.2	6.4	1412			174		0.5	182		15.7	1.2
477		0.2	4.0				145		0.5	191		12.2	0.8
590			2.3							185		9.5	
360			3.5							180		9.4	
277			4.1							189		7.5	
222			4.6							311		4.3	
207			4.3							256		4.9	
212			4.8							271		4.4	
282			2.9							253		4.2	
252			2.1							254		3.8	
270			1.3							223		3.7	

The average results for a soil containing mixtures of sodium chloride, sodium carbonate, and sodium sulfate and for natural alkali soils are given in table 9. These soils were similar in the order in which they parted with their soluble

salts. The first washings carried away most of the chloride and sulfate. Often the first water leached through the soil was nearly saturated with salt. The carbonate, both in the natural alkali soil and the synthetic soil, was rapidly leached from the soil during the first period, but later it was only slowly removed. The slow leaching of sodium carbonate from the soil was due to two factors, viz., (a) the extremely bad physical condition of the soil and (b) the chemical combination or adsorption of the black alkali by the various colloidal constituents of the soil. The second factor was of the greater importance, for table 4 shows that although the black alkali soil leached extremely slowly as compared with the white, yet the speed of leaching did not decrease after long periods of leaching. The quantity of sodium carbonate, which the drainage water was carrying from the soil, was very small even though the soil still contained great quantities of sodium carbonate, as may be seen from table 10.

TABLE 10
Recovery of salts from prepared and natural alkali soils

SOIL	TREATMENT			NaCl RECOVERED		Na ₂ SO ₄ RECOVERED		Na ₂ CO ₃ RECOVERED	
	NaCl	Na ₂ SO ₄	Na ₂ CO ₃	gm.	per cent	gm.	per cent	gm.	per cent
College.....	180			128.9	71.6				
		180				159.9	88.8		
			180					120.5	66.9
	90		90	85.0	94.5			22.0	24.5
	90	90		85.0	94.5	86.0	95.6		
		90	90			83.0	92.2	19.4	21.6
Corinne.....	60	60	60	54.8	91.3	58.6	97.7	26.0	43.3
Richland Acres.....				379.1		6.3			
Benson Ward.....				12.7		67.8			
				97.0		40.6		103.7	

Eighty-four liters of water passed through the soil containing 2 per cent of sodium chloride in 49 days and removed 71.6 per cent of the sodium chloride from the soil. One hundred and seventy-five liters leached through the soil treated with 2 per cent sodium sulfate in 29 days and removed 88.8 per cent of the sulfate from the soil, whereas only 140 liters of water drained through the soil treated with carbonate in 274 days and removed 66.9 per cent of the sodium carbonate from the soil.

It is evident from these results that the speed with which the water passes through the soil and the ease with which the salts are removed is a function of the kind and the quantity of salt within the soil. It is greatest in the sulfate and least in the carbonate.

A mixture of sodium chloride and sodium carbonate leached more slowly than either of the salts separately. In 640 days only 93 liters of water passed through soil treated with these two salts and removed 24.5 per cent and 94.5 per cent, respectively. Sodium sulfate in every case accelerated the

speed with which water passed through the soil and also the rate with which the chloride was removed. But even in the presence of sulfate, sodium carbonate was leached from the soil extremely slowly. During the leaching 88.8–97.7 per cent of the sulfate was removed from the soil, 71.6–94.5 per cent of the sodium chloride, and only 21.6–66.9 per cent of the sodium carbonate. It is evident from the results as a whole that the prepared alkali soil containing sodium chloride, sodium sulfate, and sodium carbonate reacts very similarly to the natural alkali soil. In each case the carbonate was the substance giving the difficulty, as was the case in each of the natural soils tested.

CALCIUM AND MAGNESIUM CONTENT OF LEACH WATER

All four soils were high in calcium and magnesium. The College Farm soil, which is normally free from alkali and which has been used in all of this work for the preparation of the prepared alkali soil, contained 33.31 per cent of acid soluble material. It contains 7.41 per cent of calcium oxide and 4.15 per cent of magnesium oxide. This is a calcium-magnesium ratio of 7:4 which is the ratio Loew and May (13) found to be best for the germination and growth of cereals. They were, however, dealing with soluble calcium and magnesium, whereas this is mainly in the insoluble form, much of it probably being in the form of the double salt $\text{CaMg}(\text{CO}_3)_2$. The question naturally arises as to the order in which these two bases are dissolved out by water both in the absence and presence of the various alkali salts. To answer this, all of the drainage waters were analyzed for calcium and magnesium. The average results for the variously treated soils are given in table 11. The drainage water was analyzed when approximately 2000 cc. had leached from the soil.

A number of very interesting features appear in these results. For instance, the calcium magnesium ratio for salts leached from untreated soil is narrow, averaging 1.2–1.0 which is ideal according to the findings of Furuta (6), Aso (1, 2), Bernardini and Corso (3), and Bernardini and Siniscalchi (4) for wheat, rye, oats, and other plants with small leaf surface. The constant leaching of these soils by water, judging from the order in which the lime and magnesia are being carried out, should never leave them toxic because of a wrong lime-magnesia ratio.

On the other hand, the soil which was treated with 2 per cent sodium chloride yielded large quantities of calcium in the early leach water, probably because of the formation of calcium chloride and sodium carbonate. This gave a very wide lime to magnesia ratio, which was as wide as 7.1 to 1 in some of the drainage waters. As the soluble salts were washed from the soil the ratio became narrow and toward the last was as low as 1 to 3, which according to Loew and his coworkers (13) would cause a very unproductive nutritive medium for the growth of plants. It would therefore seem that the long unproductive period following the drainage of alkali soil is due at times to a toxic lime-magnesia ratio of the soil solution and should be rectified by the addition of lime to the soil. The lime would not only cause a better state

TABLE 11

Calcium oxide, magnesium oxide, and lime magnesia ratio in drainage from treated soils and natural alkali soils

LEACH- ING	NO SALT			2 PER CENT NaCl			2 PER CENT Na ₂ SO ₄			2 PER CENT Na ₂ CO ₃			1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄			1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃		
	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
1	4.6	3.0	1.5	60.4	19.9	3.1	13.5	15.1	0.9	2.0	0.8	2.5	18.5	12.6	1.5	2.1	1.8	1.2
2	1.2	1.5	0.8	56.4	17.4	3.2	11.1	6.8	1.6	2.5	0.8	3.1	18.6	12.9	1.4	2.4	1.7	1.4
3	0.7	1.5	0.5	31.1	4.1	7.1	7.2	2.3	3.1	1.7	0.4	4.2	8.9	3.5	2.5	2.3	1.3	1.8
4	2.1	1.0	2.1	1.4	2.9	0.5	3.9	1.0	3.9	1.5	0.2	7.5	3.1	1.5	2.1	1.4	0.6	2.3
5	0.5	0.5	1.0	0.8	2.3	0.3	2.6	0.6	4.3	1.2	0.3	4.0	2.0	0.8	2.5	1.2	1.0	1.2
6	0.6	0.4	1.5	0.5	1.5	0.3	1.9	0.4	4.8	1.2	1.2	6.0	1.4	0.5	2.8	1.2	0.5	2.4
7							2.2	1.3	1.7	0.8	0.2	4.0	1.2	0.5	2.4			
8							1.4	0.3	4.7	0.9	0.2	4.5	0.8	0.5	1.6			
9							1.3	0.7	2.0									
10							1.3	0.5	2.6									
11																		
12																		
13																		
Total....	9.2	7.9	1.2	150.6	48.1	3.2	46.4	29.0	1.6	11.8	3.1	3.8	54.5	32.8	1.7	10.6	6.9	1.5

TABLE 11—Continued

LEACH- ING	1 PER CENT Na ₂ SO ₄ + 1 PER CENT Na ₂ CO ₃			0.66 PER CENT EACH NaCl, Na ₂ SO ₄ , Na ₂ CO ₃			CORINNE SOIL			RICHLAND ACRES SOIL			RENSON WARD SOIL		
	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO	CaO	MgO	CaO MgO
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
1	2.5	2.0	2.3	9.9	6.8	1.5	26.3	73.2	0.3	14.6	65.0	0.2	0.6	0.4	1.5
2	3.6	2.4	1.5	6.0	2.5	2.4	2.6	6.0	0.4	1.5	17.6	0.1	6.7	0.6	11.1
3	3.3	0.9	3.7	2.1	0.7	3.0	1.2	9.8	0.1	1.2	1.2	1.0	2.9	0.5	5.8
4	1.0	0.5	2.0	1.1	0.5	2.2	1.1	0.6	1.9	0.8	1.0	0.8	1.1	0.5	2.2
5	1.7	0.6	2.8	1.1	0.6	1.8	2.0	1.1	1.9	0.5	1.1	0.5	0.8	0.5	1.6
6	1.1	0.5	2.2	1.0	0.4	2.5				0.6	0.5	1.2	1.1	0.5	2.2
7				1.0	0.3	3.3							0.7	0.3	2.3
8				1.0	0.6	1.8							0.6	0.2	3.0
9				0.9	0.3	3.0							0.7	0.3	2.3
10				0.7	0.2	3.5							0.7	0.3	2.3
11				1.0	0.3	3.3							0.6	0.1	6.0
12				1.0	0.5	2.0							0.5	0.2	2.5
13				1.9	0.6	3.1									
Total...	13.2	6.9	1.9	28.7	14.3	2.0	33.2	24.7	1.3	19.2	86.4	0.2	17.0	4.4	3.9

of tilth but also a proper lime-magnesia ratio. The rapid removal of the calcium as opposed to the magnesium from the soil may also yield a soil deficient in total calcium as compared to total magnesium. It is quite conceivable that this may occasionally occur when chlorides are used over long periods in commercial fertilizers.

Soil containing 2 per cent of sodium sulfate yielded more calcium and magnesium in the leach water than did untreated soil, but only 30 and 60 per cent, respectively, as much as was yielded by soil treated with sodium chloride. The lime-magnesia ratio was narrow in the first leaching and wider later. However, the average ratio for the entire leaching was 1.6 to 1, and it never became narrow enough to indicate a toxic condition. Moreover, the speed with which the two salts were carried from the soil was such that the ratio in the soil would not be upset enough to render it toxic. Hence, viewed in the light of these results fertilizers containing sulfates would probably be safer in long continued experiments on this soil than would fertilizers containing chlorides.

Less magnesium and only slightly greater quantities of calcium were leached from soil treated with sodium carbonate than from untreated soil. There was a wide calcium-magnesium ratio throughout the leaching process and no indication that the toxic ratio would be reached in soil containing black alkali. It is significant that thirteen times as much calcium and fifteen times as much magnesium was carried away in drain water where sodium chloride was the alkali present as where sodium carbonate was the salt present.

Soil containing a mixture of sodium chloride and sodium sulfate lost more calcium and magnesium than soil containing only sodium sulfate and considerable less than the same soil containing only sodium chloride. The lime-magnesia ratio was 1.7 to 1 which does not indicate toxicity as is the case in the last leaching from soil treated with sodium chloride.

Soil containing mixtures of sodium chloride and sodium carbonate and of sodium sulfate and sodium carbonate parted with their calcium slowly and as an average lost no more than the untreated soil. In every case the quantity of calcium exceeded the quantity of magnesium and usually with a margin great enough to render the solution non-toxic according to Loew's lime-magnesia theory.

Because of the extremely long time necessary to leach the soil containing the three salts, this series lost more calcium and magnesium than did the untreated soil or those soils containing only a single salt. The excess loss of calcium over that of magnesium was most noticeable here.

The quantity of calcium lost from the Corinne soil was about the same as that leached from the prepared alkali soil. However, the magnesium lost from the Corinne soil was much greater and the quantity of magnesium in the leachings greatly exceeded the quantity of lime. This was due to the large quantities of soluble magnesium chloride and sulfate in the original soil and it cannot be assumed that magnesium carbonate was rendered soluble. This

was true in both the Corinne and Richland Acres soil from which a great excess of magnesium over calcium left the soil in the first drain waters. In the Benson Ward soil the lime-magnesia ratio was wide throughout with only small quantities of the salts leached from the soil.

PHOSPHORUS CONTENT OF DRAINAGE WATERS

The drainage waters from each pot were analyzed for phosphorus and the average results are given in table 12. Analyses were made on each bottle which contained approximately 2000 cc. of the leach water. This fractional analysis gives the order in which the phosphorus left the soil. It is interesting to note that not only while the large quantities of alkali were leaving the soil

TABLE 12
Phosphorus leached from synthetic and natural alkali soils

LEACHING		2 PER CENT NaCl	2 PER CENT Na ₂ SO ₄	2 PER CENT Na ₂ CO ₃	1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄	1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃	1 PER CENT Na ₂ SO ₄ + 1 PER CENT Na ₂ CO ₃	0.66 PER CENT EACH NaCl Na ₂ SO ₄ Na ₂ CO ₃	CORINNE SOIL	RICH- LAND ACRES SOIL	BENSON WARD SOIL
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	3.81	3.49	18.30	323.20	7.70	15.28	20.61	7.05	8.18	1.89	805.98
2	4.48	6.68	18.86	139.00	11.16	38.70	37.95	25.11	12.73	5.50	144.00
3	5.06	26.43	10.16	54.20	12.91	37.89	28.46	24.86	16.86	2.95	69.46
4	6.48	35.18	8.69	34.39	10.27	28.54	19.44	23.77	22.49	3.14	35.16
5	4.35	34.50	13.97	28.49	16.36	27.16	22.20	23.18	19.54	1.76	22.75
6	4.65	20.81	11.12	26.07	18.67	27.93	21.65	22.74			19.40
7			8.42	25.16	19.40			22.24			13.79
8			5.87	21.02	15.32			20.24			11.16
9			6.85	19.02	21.26			21.50			9.85
10					14.99			20.25			9.60
11								18.90			7.70
12								17.42			6.42
13								17.88			
Total . . .	28.83	127.09	102.24	670.54	148.04	175.50	150.31	265.14	79.80	15.24	1155.27

but even toward the end of the leaching period large quantities of phosphorus were leaving in the drainage water.

One may conclude from these results that the long unproductive period following the leaching of alkali soil cannot be due to the lack of available phosphorus, for the alkali soils are yielding one to five times as much water-soluble phosphorus as are productive soils. It is, however, the more easily available phosphorus which is being taken from the soil and it is quite possible that after considerable leaching and the removal of the greater part of the soluble salt the water-soluble phosphorus may be very low. Moreover, the bacterial activities which tend to render it soluble are low. Hence, for a time after leaching alkali soil may be low in easily available phosphorus.

The carbonate liberated the largest quantities of phosphorus, the chloride less, and the sulfate least. Even the sulfate liberated appreciable quantities. If we consider the removed phosphorus from the untreated soil as 100, the amount removed from soil treated with sodium sulfate is 355; with sodium chloride, 441; with sodium carbonate, 2325; with sodium chloride and sodium sulfate, 514; with sodium sulfate and sodium carbonate, 521; with sodium chloride and sodium carbonate, 609; and with the mixture of the three salts, 92. The Benson Ward soil yielded considerably more phosphorus than any of the synthetic alkali soils. The other two natural alkali soils yielded smaller quantities of phosphorus. This substantiates the theory which was argued at some length by the senior author elsewhere (10)—that the beneficial action of some common soil amendments is due largely to their solvent action on insoluble plant-food and that this is especially marked in the case of the phosphorus. Crops grown on soil treated with chlorides and sulfates often yield more heavily and the phosphorus content of the plant is usually greater than where the chloride or sulfate is not added to the soil. Wherever soil is deficient in available phosphorus this should occur; hence, it accounts for the common phenomenon of no increase where chlorides or sulfates are added to soil already supplied with available phosphorus. Moreover, these salts often exert another effect, that of increased bacterial activity which increases available nitrogen since it has been shown that these salts increase ammonification (8), nitrification (11), and azofication (12). It is often hard to show that there is an increase of water-soluble phosphorus in soil treated with soluble salts (7). This, as has been shown elsewhere (10), is often due to rapid metabolism of phosphorus by the microflora of the soil by which it is changed to insoluble organic compounds. This would not, however, have occurred in this soil since the bacterial activities of the soil have been shown to be very materially reduced by these concentrations of salts (9). Therefore, the effect which is noted here is due to the direct solvent action of the soil solution upon the inorganic phosphates and to the action of sodium carbonate upon the organic phosphorus of the soil. However, when the concentration of salt is low its stimulating influence upon the microflora would result in increased acids which would have an appreciable influence on the soluble plant-food of the soil.

POTASSIUM CONTENT OF DRAINAGE WATERS

Total potassium determinations were made on each fraction of the drainage water and the average results are given in table 13. The early leachings from all the prepared and natural alkali soils were very rich in potassium as compared with non-alkali soil. Of the soils treated with only one salt the greatest quantities of potassium were rendered soluble by the chloride, less by the sulfate, and least by the carbonate. It is evident that soil such as this would respond greatly to soil amendments which would render available large quantities of potassium. The mixtures of the salts in all cases were more

effective than the single salt. In all of the natural alkali soils large quantities of potassium were found in the leachings at first, but it is significant that as leaching continued in all the soils the quantity of potassium in the drainage water very materially decreased. In some cases very small quantities were being removed in the leach waters. These results point strongly to the conclusion that the unproductive period following the leaching of alkali soil is due, in a measure, to a lack of available potassium. The addition of organic matter to such a soil not only causes better tilth but increases bacterial activity, and the increased bacterial activity should result in more available potassium. The excess losses of soluble potassium from these alkali soils must have been due to a direct solvent action of the salt and not to increased bacterial action.

TABLE 13
Potassium leached from synthetic and natural alkali soils

LEACHING	SOIL	2 PER CENT NaCl	2 PER CENT Na ₂ SO ₄	2 PER CENT Na ₂ CO ₃	1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄	1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃	1 PER CENT Na ₂ SO ₄ + 1 PER CENT Na ₂ CO ₃	0.66 PER CENT EACH NaCl Na ₂ SO ₄ Na ₂ CO ₃	CORINNE SOIL	RICH- LAND ACRES SOIL	BENSON WARD SOIL
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	65.4	259.2	137.9	114.9	269.4	183.8	132.2	270.9	1965.0	535.0	266.4
2	37.9	254.8	68.8	64.6	364.3	103.8	153.0	162.2	538.0	253.6	155.8
3	44.7	17.4	69.5	41.3	80.6	83.9	112.0	59.1	144.6	117.5	99.6
4	36.1	15.1	35.7	18.3	54.3	52.5	60.3	61.9	117.8	158.2	82.3
5	31.8	13.8	28.7	13.1	44.7	55.4	64.6	57.3	90.1	71.6	57.6
6	30.5	2.0	20.7	17.5	36.6	53.5	62.8	60.2		55.8	48.1
7			38.1	37.2	16.1			35.8			45.3
8			14.7	26.4	28.7			31.0			39.7
9			10.6	21.7	36.1			23.9			37.1
10								16.1			38.1
11								18.4			29.3
12								20.5			29.3
13								1.5			
Total....	246.4	563.0	423.8	355.0	930.8	532.9	584.9	818.8	2855.5	1191.7	928.6

NITROGEN CONTENT OF LEACHINGS

Determinations for nitrogen were made on composite samples of the leach water. The results given in table 14 correspond to the totals given in previous tables.

In every case the salt-treated soil lost more nitrogen than the untreated soil. The sulfate-treated soil yielded nearly twice as much, the chloride-treated nearly five times, and the carbonate-treated soil nine times as much as the untreated soil. Most of the nitrogen was in the form of organic material and the weak salt solution, which was a good protein solvent, carried out large quantities. It is significant that the chloride and especially the carbonate, both of which are hard to leach from the soil and leave it in a very bad state of

tilth, carried out the greater quantity of organic nitrogen. The natural alkali soils, except for the Benson Ward soil which contained large quantities of nitrates, yielded less nitrogen than most of the synthetic alkali soils. There is no relationship between the phosphorus and nitrogen of the soil except where sodium carbonate was applied to the soil. This indicates that it is the inorganic phosphates which are being rendered soluble and carried from the soil by the salts and not the phosphoproteins and nucleoproteins, as was the case with sodium carbonate. The phosphorus-nitrogen ratio varied from 1 to 1.3 in the case of soil treated with sodium chloride and sodium sulfate to 1 to 7.2 in the soil treated with sodium carbonate and sodium sulfate.

TABLE 14
Nitrogen leached from synthetic and natural soils

SOIL	TREATMENT	NITROGEN IN TOTAL LEACH WATER
		<i>mgm.</i>
College	Untreated	119.8
	2% NaCl	558.1
	2% Na ₂ SO ₄	279.3
	2% Na ₂ CO ₃	2666.2
	1% NaCl + 1% Na ₂ SO ₄	498.1
	1% NaCl + 1% Na ₂ CO ₃	948.1
	1% Na ₂ CO ₃ + 1% Na ₂ SO ₄	1096.2
	0.66% each NaCl, Na ₂ SO ₄ , Na ₂ CO ₃	673.6
Corinne		334.2
Richland Acres		225.0
Benson Ward		1267.7

ORGANIC CARBON CONTENT OF LEACHINGS

The carbon content of the drainage waters was determined by the chromate methods (15). Considerable difficulty was experienced in obtaining concordant duplicates and the results obtained were not very satisfactory. Table 15 shows that the organic carbon content of the untreated soil was quite constant in each fraction of the leach water, but in all the salt-treated soil the first drainage water was much richer in carbon than later fractions. The salts apparently rendered it soluble so it readily leached from the soil and left the soil almost devoid of organic matter. Soil treated with sulfate lost no more organic carbon than the untreated soil, whereas soil treated with chloride and carbonate lost large quantities of organic matter.

The carbon-nitrogen ratio was wide in the leachings of the untreated soil and narrow in the alkali soil which indicates that the organic material carried away in the drainage water was proteinaceous. The black alkali soil yielded a drainage water which was very rich in nitrogen as compared with its carbon. It probably lost most of its readily ammonifying material and retained carbonaceous material which would be attacked only slowly by the microflora of the soil.

RELATIVE AMOUNTS OF PLANT NUTRIENTS LOST BY LEACHING

That the drainage water of the prepared alkali soil was rich in valuable plant nutrients is brought out in table 16 in which the losses from the untreated soil are taken as 100.

In three of the salt treatments less magnesia was extracted than in the untreated soil, and in one case less carbon was extracted where salt was present.

TABLE 15

Carbon content and carbon-nitrogen ratio of leachings from synthetic and natural alkali soils

SOIL	TREATMENT	CARBON IN LEACHINGS	CARBON-NITROGEN RATIO IN LEACHINGS
		mgm.	
College	Untreated	2566	21.4:1
	2% NaCl	5131	9.1:1
	2% Na ₂ SO ₄	2439	8.7:1
	2% Na ₂ CO ₃	9414	3.5:1
	1% NaCl + 1% Na ₂ SO ₄	6703	13.4:1
	1% NaCl + 1% Na ₂ CO ₃	9176	9.7:1
	1% Na ₂ SO ₄ + 1% Na ₂ CO ₃	9591	8.8:1
	0.66% each NaCl, Na ₂ SO ₄ , Na ₂ CO ₃	11607	17.2:1
Corinne		762	2.3:1
Richland Acres		1777	7.9:1
Benson Ward		16408	13.0:1

TABLE 16

Plant nutrients in leachings from synthetic alkali soil

ELEMENT	UN-TREATED SOIL	SOIL + 2 PER CENT NaCl	SOIL + 2 PER CENT Na ₂ SO ₄	SOIL + 2 PER CENT Na ₂ CO ₃	SOIL + 1 PER CENT EACH NaCl Na ₂ SO ₄	SOIL + 1 PER CENT EACH NaCl Na ₂ CO ₃	SOIL + 1 PER CENT EACH Na ₂ SO ₄ Na ₂ CO ₃	SOIL + 0.66 PER CENT EACH NaCl Na ₂ SO ₄ Na ₂ CO ₃
Calcium.....	100	1637	504	128	592	115	143	312
Magnesium.....	100	609	367	39	415	87	87	155
Phosphorus.....	100	441	355	2325	514	609	521	920
Potassium.....	100	229	172	144	378	216	237	332
Nitrogen.....	100	466	233	223	416	791	910	562
Carbon.....	100	200	95	367	261	358	374	452

In all other cases the salt increased the solubility of the tested constituent. Twenty-three times as much phosphorus was extracted from soil treated with 2 per cent of sodium carbonate as was lost from the check. Although most of this phosphorus came from the insoluble phosphates, yet the large quantities of carbon, nitrogen, and phosphorus extracted in the presence of sodium carbonate makes it appear certain that in this treatment much of the organic phosphorus is being carried from the soil in the drainage waters.

SUMMARY

The soils used in this work were three natural alkali soils: one in which the chlorides predominated, a second in which the sulfates predominated, and a third which was heavily charged with sodium carbonate. A productive calcareous silt loam was also used. This was made into an alkali soil by various treatments with sodium chloride, sulfate, and carbonate.

These were leached in 2-gallon jars until the greater portions of the salts were removed. The amount of leaching required is given in table 6.

The natural alkali soil behaved similarly to the non-alkali soil treated with a mixture of the salts. Soil treated with sodium carbonate leached very slowly and after leaching was in very bad tilth. The soil treated with sodium chloride leached more readily than the sodium carbonate soil but was slow as compared with the natural soil and remained in a bad physical condition. The soil treated with sodium sulfate leached rapidly and was left in fair tilth.

Sodium sulfate leached readily from the soil and the first drainage water was nearly saturated; 88.8-97.7 per cent of the sulfate was leached from the soil. The first water passing through the soil treated with sodium chloride was heavily charged with chloride and 71.6-94.5 per cent of the chloride was recovered in the drainage water. Soil treated with sodium carbonate leached very slowly; toward the end in one case the rate per hour was one cubic centimeter containing only 0.07 mgm. of sodium carbonate. From 21.6 to 66.9 per cent of the added carbonate was recovered in the leach water. It was therefore impossible by the leaching process to free a column of soil one foot in depth and provided with ideal underdrainage from sodium carbonate to such an extent that crops would grow upon it. This was due to two factors: (a) Sodium carbonate breaks down the structure of a fine-grained soil to such an extent that it is rendered almost impervious to water; (b) the sodium carbonate is held so firmly by the colloidal material that it cannot be washed out by water.

From 1.2 to 16.4 times as much lime was leached from alkali soil as from normal soil which shows that the various salts greatly increased the solubility of calcium. This effect was least in the case of sodium carbonate and greatest in the case of sodium chloride. From 0.4 to 6 times as much magnesium was leached from treated soil as from untreated soil. The order of solubility is the same as that of lime. The order with which the two ions, calcium and magnesium, leave the soil make it possible for some soils to be left after leaching with a toxic lime-magnesium ratio and it is probable that at times the addition of lime to a drained alkali field benefits the soil in two ways, (a) by improving the tilth due to the flocculant action of the lime and (b) by causing a productive lime-magnesia ratio.

From 3.6 to 23.3 times as much phosphorus was leached from the treated soil as from the untreated soil. This excess was greatest when sodium carbonate was added to the soil and least when sodium sulfate was applied. Most of

it was due to the direct action of the salt on the insoluble inorganic phosphorus of the soil. However, a study of the carbon-nitrogen-phosphorus content of the drainage waters from soil treated with sodium-carbonate indicated that considerable quantities of organic phosphorus were carried out in the drainage waters of the soil treated with sodium carbonate.

The potassium content of the treated soil was 1.5–3.8 times as great as that of the untreated soil. The greatest quantity was found in the leachings from soil treated with sodium chloride and least in soil treated with sodium carbonate.

The nitrogen content of the treated soil after leaching was 2.2 to 9.1 times that of the untreated soil and the carbon content, 1 to 4.5 times. This difference in losses shows that proteinaceous material was rendered soluble.

The results substantiate the theory argued by the senior author in a former paper—that soil amendments often make more plant-food soluble, especially phosphorus and nitrogen.

The results make it appear likely that the long unproductive period following the drainage of alkali soil is caused by (a) the leaching of much of the readily available plant-food which makes necessary a period of weathering before sufficient plant-food is available for crop production, (b) the poor state of tilth of the drained soil and sometimes (c) a toxic lime-magnesia ratio.

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THE EFFECT OF PLANTS ON THE CONCENTRATION OF DRAINAGE WATER FROM THE CORNELL LYSIMETERS

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A slight change in the method of handling the aliquot samples of drainage water from the Cornell lysimeters has resulted in the analysis of the percolates for total solids at various times during the year. It is the purpose of this paper to present the concentration of the leachings from certain of the planted and unplanted lysimeters, over a period of three years. The results from eight of these will suffice to show the effect that plants have had on the concentration of the percolated water from two distinct types of soil.

Since the lysimeters and the soils with which they are filled have been fully described by Lyon and Bizzell (1, 2), it will not be necessary to repeat their descriptions here.

Six of the eight lysimeters selected were filled with Dunkirk clay loam soil in 1909. Two of these have been kept free of vegetation, two in grass continuously, and two have been planted to a five-year rotation of maize, oats and wheat followed by two years of hay. One of each of these three pairs of tanks has received an application of burnt lime at the beginning of each rotation and all of them have received farm manure. Results from two of the lysimeters filled with Volusia silt loam soil are also presented. One of these has been kept bare while the other has been cropped to the rotation already cited. These tanks were filled in 1910 and they have received applications of burnt lime and farm manure. These treatments are summarized in table 1.

Numerous experiments have been conducted in various ways in an attempt to determine the concentration of the soil solution and the extent to which it is affected by growing plants. The literature on this subject has been reviewed rather fully by Stewart (3) who came to the conclusion that the results which have been obtained are contradictory in nature. In analyzing water extracts of thirteen soils of two different types for certain of its constituents through two seasons, Stewart found that during the second season there were notable differences between the concentrations from cropped and uncropped soil, the latter being more concentrated. He also found that there were large differences between the soluble nutrients present in the extracts from uncropped soils.

The writer has found the conclusions drawn by Stewart regarding the greater quantities of nitrates, calcium, potassium and magnesium in the extracts from cropped and uncropped soils, made at various times throughout the year,

to hold for the concentration of soluble material in the percolates from soil tanks.

TABLE 1
Treatment of soil in lysimeters

TANK	SOIL	TREATMENT OF SOIL		
		Fertilizer	Lime	Crop
3	Dunkirk clay loam	Farm manure	None	Rotation
4				Grass
6				None
7	Dunkirk clay loam	Farm manure	Burnt lime	Rotation
8				Grass
10				None
15	Volusia silt loam	Farm manure	Burnt lime	Rotation
16				None

TABLE 2
Average percolation concentration and loss of soluble material from planted and unplanted lysimeters, filled with Dunkirk clay loam soil, from May 1, 1920 to May 1, 1921

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE
		May 1-Dec. 1		Dec. 1-Mar. 15		Mar. 15-May 1		Average for two tanks	Per acre	
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration			
		liters	p.p.m.	liters	p.p.m.	liters	p.p.m.	gm.	lbs.	liters
3, 7	Maize	119	358	187	290	69	332	120	660	375
4, 8	Grass	110	441	163	358	80	372	137	751	353
6, 10	Bare	378	512	185	406	78	474	305	1,677	641

TABLE 3
Average percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Dunkirk clay loam soil, from May 1, 1921 to May 1, 1922

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE
		May 1-Dec. 1		Dec. 1-Feb. 24		Feb. 24-May 1		Average for two tanks	Per acre	
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration			
		<i>liters</i>	<i>p.p.m.</i>	<i>liters</i>	<i>p.p.m.</i>	<i>liters</i>	<i>p.p.m.</i>	<i>gm.</i>	<i>lbs.</i>	<i>liters</i>
3, 7	Oats	96	315	88	256	274	251	122	668	358
4, 8	Grass	159	389	92	303	296	277	172	944	547
6, 10	Bare	303	564	115	471	275	581	385	2,120	693

The concentrations of the drainage water from the lysimeters containing Dunkirk clay loam soil are shown in tables 2, 3 and 4. Each table presents

the results for a single year and for different periods during the year. The periods are quite variable in length since they are dependent on the flow from the planted tanks, which in turn is regulated by climatic conditions and the crop grown. It may be seen at once from the tables that the average concentration of percolates, expressed in parts per million of soluble material, from the bare soils is considerably higher than that from the soils which have been in rotation. The rotation crop for 1920 was maize; for 1921, oats; and for 1922, wheat.

Not only is the concentration of the drainage water from the bare soil greater than that from the planted soil during the growing period of the plant but it continues to be greater year after year for each period shown in the tables. It is interesting to note that the point of lowest concentration for the bare soil percolates each year is greater than the highest concentration for the soil planted to a crop rotation.

TABLE 4

Average percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Dunkirk clay loam soil, from May 1, 1922 to May 1, 1923

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE
		May 1-Sept. 1		Sept. 1-Mar. 1		Mar. 1-May 1		Average for two tanks	Per acre	
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration			
		liters	p.p.m.	liters	p.p.m.	liters	p.p.m.			
3, 7	Wheat	139	244	113	276	249	226	121	667	501
4, 8	Grass	175	352	119	325	279	234	166	910	673
6, 10	Bare	336	562	103	481	267	342	330	1,813	706

After the crop is removed from the planted tanks and with the retarded drainage of the winter months and often its entire absence for several weeks at a time, it would seem that the concentration of the leachings from the cropped soil would be relatively higher as compared with that for the leachings from the bare soil because of the opportunity in point of time for an equilibrium adjustment between the soil material and the soil water. If such an adjustment occurred it most likely would be reflected in the early spring drainage. The absence of such an adjustment is clearly shown by the wide differences in the concentration of the water from the cropped and bare soils for the periods which include the months of March and April. This is in accord with the findings of Hoagland (4) who has presented evidence to oppose the theory that there is an immediate restoration of equilibrium when the soil solution is depleted of its soluble material by the plant or other agency. The data given here would tend to prove that this equilibrium is never reached as long as a crop is allowed to grow on the soil for a portion of each year.

The nitrate nitrogen is always more concentrated in the drainage from the bare soil than in that from the cropped soil. This fact suggests that the greater concentration of total solids in the percolates from the bare soil during the early spring might be attributed to a greater solvent action due to this greater nitrate concentration. However, when the average concentrations of nitrate nitrogen in the leachings from the bare and cropped soils were calculated to calcium nitrate and these values subtracted from the total concentrations of the water for the corresponding soils, the resulting figures, while slightly lower and farther apart than the ones appearing in the tables, showed the percolates to be of the same relative strengths.

Lyon and Bizzell (1) have found that cropping this soil conserved an amount of calcium much greater than the combined conservations of magnesium, sulfur, sodium and potassium. Since phosphates and carbonates are never present in quantities large enough to be of any importance, and since bicarbonates are of about equal strength in the leachings from the cropped and uncropped soils it would seem that most of the nitrate radical would be associated with calcium. In view of these facts the calculation as made above appears justified.

The tables also show that the concentrations of the percolates are more or less independent of the amount of water which passes through the soil. Irrespective of the quantity of drainage from the several tanks, the concentration of that from the bare soil is always highest, that from the soil planted to a crop rotation always lowest, while that from the tanks which are in grass continuously is intermediate. Since the volume of water passing through the tanks is not the determining factor of its concentration it is probable that the soils have reached a stage where a somewhat definite quantity of soluble material is relinquished to the movable water through them and that this quantity is liberated regardless of whether the normal precipitation, which the lysimeters receive, permeates them quickly or slowly.

In most cases the concentration of the percolates are seen to decrease as the seasons progress from the month of May but they regain their former strengths with each succeeding year.

The analyses of the drainage from the Volusia silt loam soil are given in tables 5, 6 and 7. It will not be necessary to point out the facts revealed in these tables beyond the statement that they serve to substantiate the conclusions that have been drawn from the Dunkirk clay loam soil. It may be added, however, that the concentrations of the percolates from the last named soil are higher than those from the Volusia silt loam.

The collective data from the two soils here presented bring out two points rather conclusively: first, that the concentration of the percolates from the lysimeters is not dependent on the quantity of water leaching through the soils; and second, that the different soil treatments result in bringing about a condition within the soils which causes them to liberate their soluble material in a more or less characteristic way.

It is quite possible that the colloidal material in the soil and the water film which is in intimate contact with the soil particles relinquish a rather definite proportional share of their soluble material to that portion of the soil water

TABLE 5

Percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Volusia silt loam soil, from May 1, 1920 to May 1, 1921

TANK	SOIL TREAT- MENT	DRAINAGE WATER								SOLIDS REMOVED		TOTAL DRAINAGE
		May 1-Sept. 1		Sept. 1-Dec. 1		Dec. 1-Mar. 15		Mar. 15-May 1		From tank	Per acre	
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration			
		liters	p.p.m.	liters	p.p.m.	liters	p.p.m.	liters	p.p.m.	gm.	lbs.	liters
15	Maize	158	261	277	243	247	234	127	249	198	1,089	809
16	Bare	183	482	184	441	181	317	92	322	256	1,408	640

TABLE 6

Percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Volusia silt loam soil, from May 1, 1921 to May 1, 1922

TANK	SOIL TREAT- MENT	DRAINAGE WATER								SOLIDS REMOVED		TOTAL DRAINAGE
		May 1-Oct. 1		Oct. 1-Dec. 1		Dec. 1-Feb. 24		Feb. 24-May 1		From tank	Per acre	
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration			
		liters	p.p.m.	liters	p.p.m.	liters	p.p.m.	liters	p.p.m.	gm.	lbs.	liters
15	Oats	130	254	331	240	273	212	448	205	262	1,442	1,182
16	Bare	205	390	295	429	299	250	441	279	404	2,223	1,240

TABLE 7

Percolation, concentration and loss of soluble material from planted and unplanted lysimeters filled with Volusia silt loam soil, from May 1, 1922 to May 1, 1923

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE
		May 1-Sept. 1		Sept. 1-Mar. 1		Mar. 1-May 1		From tank	Per acre	
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration			
		liters	p.p.m.	liters	p.p.m.	liters	p.p.m.	gm.	lbs.	liters
15	Wheat	458	248	431	242	345	182	281	1,545	1,234
16	Bare	564	376	358	282	285	225	377	2,074	1,207

which is free to move. This assumption would help to explain why the concentration of the soil solution, as measured by Bouyoucos and McCool (5) and others, differs from that ordinarily found in soil extracts and in the drainage water from lysimeters.

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STUDIES ON VIRGIN AND DEPLETED SOILS¹

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The actual changes in several important respects which a soil undergoes in passing from a virgin to a depleted condition have not been investigated to any great extent.

It is quite generally conceded that the supply of available plant food elements as well as the content of organic matter is materially decreased as a soil becomes "worn out." A number of cases have also been reported in which the total amounts of phosphorus and calcium have been reduced.

So far as the writer is aware, however, little information is at hand regarding the relative rate of change in the concentration of the soil solution of depleted and virgin soils when they are maintained at a given moisture content and temperature for various periods. The composition of solutions so obtained is unknown as well as the relative ability of virgin and badly run down soils to repeatedly give up solutes when the material in solution is removed by washing. The rôle of organic matter in maintaining the concentration of the soil solution is also uninvestigated. It is the purpose of this paper to throw some light on these questions and to set forth any relationships found to exist between the amounts of various plant food elements going into solution from a number of soils upon standing different lengths of time at different moisture contents, and the increase in plant growth resulting from addition of these elements.

REVIEW OF LITERATURE

McCool and Millar (3) determined the rate of formation of soluble material in several virgin and the corresponding depleted soils by means of the freezing point method. In general the concentration of the soil solution of the virgin soils was much greater than that of the cropped soils after a ten-day period at 25°C. At the expiration of thirty days, however, the difference had largely disappeared. A decrease in moisture content and a lower temperature also tended to decrease the difference in rate of solubility.

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Millar (5) reported a correlation between the difference in rate of solution of several depleted and virgin soils and the observed differences in productiveness. The samples were washed on ordinary filters to remove the major portion of the soluble salts before placing in the constant temperature chamber. This procedure reduced the tendency, previously reported, for the concentrations of the solutions to decrease as the period of contact was prolonged.

Shedd (8) found the total phosphorus and that soluble in 0.2 *N* HNO_3 to be greater in seventeen virgin soils than in the corresponding cropped samples.

As the result of a careful study of the phosphorus content of nine soils which had been under cultivation for 40–60 years and of corresponding virgin soils Whitson and Stoddart (12) report large losses as the result of cropping with the exception of one case. Other soils which had received large amounts of manure during cultivation of 30–62 years showed large increases in phosphorus content in a number of cases, but more than half of these contained more phosphorus in the virgin than in the cropped and manured samples.

Shedd (9) divided the soils of Kentucky into areas on a geological basis and determined the total calcium and that soluble in 0.2 *N* HNO_3 and in carbonated water in samples of cropped and virgin soils from each area. In the large majority of cases each method showed more calcium in the virgin than in the cropped soils.

Swanson and Miller (10) report the analyses of samples from long cropped areas and areas in native bluestem hay or buffalo grass pasture from several types of Kansas soils. In only two cases, however, were the cropped and virgin samples taken from areas in close proximity. The data for the two comparable soils show a decided loss in sulfur, nitrogen and carbon as a result of cropping. One shows a gain in phosphorus, one a loss of potassium and both a gain in calcium. An average of the data for all the soils shows a marked decrease in sulfur, nitrogen and carbon content and an increase in potassium and very little change in phosphorus and calcium. As a whole the results are rather unusual.

COLLECTION OF SAMPLES

The samples in general represent the surface stratum 6 to 7 inches in depth. In some cases the sampling extended to the depth of the darker colored surface soil which in some virgin timbered soils was less than 6 inches while in some sandy cultivated soils it was more.

Two samples were taken from every soil. One from a field which had been under cultivation for a considerable period of years and had decreased more or less in productivity. The other was taken from a piece of woodland or from an old line fence row which was only a short distance from the site of the first sample. The first sample is designated as cropped or depleted while the latter is referred to as the virgin or uncropped soil. Thus the two samples represent the same soil type, the only difference between them being the changes resulting from the growth and partial removal of common farm crops, in one case, and from the growth without removal of more or less virgin vegetation in the other.

The samples were taken to the laboratory, air-dried and passed through a 2 mm. screen to remove pebbles and the coarser organic material. They were then stored in suitable containers until utilized in the laboratory experiments.

The soils studied were collected from six counties in Michigan and include eleven silt loams, seventeen sandy loams, five loams, thirteen loamy sands, and two clay loams. They represent the predominating soil types in the counties sampled.

RATE OF SOLUTION OF VIRGIN AND CROPPED SOILS

The first part of the work was devoted to the study of the rate of increase in concentration of the soil solution when the samples were washed practically free of soluble salts and then maintained at a uniform temperature with a water content slightly above saturation.

TABLE 1

Rate of solution of virgin and cropped soils expressed as freezing point depressions

SOIL NUMBER	CONDITION	DAYS MAINTAINED AT 25°C.							
		0	1	2	6	10	20	40	60
Silt loams									
1	{ Cropped Virgin	°C. 0.001	°C. 0.001	°C. 0.009	°C. 0.011	°C. 0.012	°C. 0.013	°C. 0.026	°C. 0.033
		0.004	0.004	0.010	0.020	0.040	0.043	0.074	0.081
2	{ Cropped Virgin	0.000	0.009	0.010	0.013	0.026	0.029	0.038	0.017
		0.000	0.009	0.013	0.024	0.052	0.064	0.059	0.045
6	{ Cropped Virgin	0.000	0.003	0.004	0.009	0.007	0.020	0.032	0.022
		0.000	0.009	0.013	0.020	0.042	0.053	0.060	0.041
7	{ Cropped Virgin	0.000	0.005	0.005	0.010	0.010	0.020	0.043	0.023
		0.000	0.009	0.013	0.020	0.042	0.053	0.060	0.041
Sandy loams									
14	{ Cropped Virgin	0.000	0.001	0.003	0.012	0.028	0.025	0.009	0.009
		0.000	0.002	0.008	0.015	0.029	0.024	0.013	0.015
15	{ Cropped Virgin	0.000	0.001	0.003	0.006	0.012	0.020	0.010	0.012
		0.000	0.001	0.021	0.034	0.045	0.049	0.021	0.025
16	{ Cropped Virgin	0.000	0.002	0.004	0.008	0.010	0.006	0.012	0.013
		0.001	0.001	0.009	0.021	0.039	0.045	0.056	0.041
18	{ Cropped Virgin	0.000	0.003	0.011	0.011	0.007	0.051	0.071	0.057
		0.000	0.006	0.013	0.025	0.030	0.079	0.070	0.052
21	{ Cropped Virgin	0.000	0.001	0.006	0.013	0.025	0.041	0.066	0.036
		0.000	0.007	0.012	0.022	0.030	0.050	0.077	0.078
Loamy sands									
28	{ Cropped Virgin	0.000	0.001	0.002	0.003	0.015	0.015	0.010	0.007
		0.000	0.008	0.003	0.023	0.030	0.033	0.026	0.027
30	{ Cropped Virgin	0.000	0.001	0.002	0.002	0.004	0.009	0.016	0.009
		0.000	0.009	0.018	0.029	0.039	0.049	0.054	0.044
31	{ Cropped Virgin	0.000	0.001	0.001	0.001	0.002	0.001	0.006	0.001
		0.000	0.011	0.019	0.035	0.043	0.063	0.067	0.054
33	{ Cropped Virgin	0.000	0.001	0.001	0.001	0.002	0.002	0.002	0.002
		0.001	0.002	0.003	0.010	0.011	0.013	0.023	0.012

TABLE 1—Continued

SOIL NUMBER	CONDITION	DAYS MAINTAINED AT 25°C.							
		0	1	2	6	10	20	40	60
Loams									
41	{ Cropped Virgin	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C
		0.000	0.002	0.008	0.014	0.020	0.029	0.035	0.037
42	{ Cropped Virgin	0.000	0.002	0.011	0.020	0.027	0.028	0.030	0.033
		0.000	0.007	0.010	0.018	0.020	0.030	0.035	0.020
43	{ Cropped Virgin	0.000	0.011	0.019	0.033	0.046	0.055	0.068	0.059
		0.000	0.001	0.001	0.004	0.011	0.012	0.027	0.030
43	{ Cropped Virgin	0.000	0.001	0.001	0.004	0.011	0.012	0.027	0.030
		0.000	0.012	0.015	0.030	0.040	0.060	0.059	0.041

It was decided to use the freezing point method of Bouyoucos and McCool (2) since this permitted rapid determination of the concentration of the soil solution directly in the soil without necessitating discarding the sample.

The procedure was as follows:

About 60 gm. of the air dry sample was placed in an ordinary filter and washed with distilled water until practically free of soluble material as indicated by the freezing point method. After draining for an hour or so the soil was removed and thoroughly mixed by stirring in a tumbler. Samples were placed in freezing point tubes which were then stoppered and placed in a constant temperature chamber at 25°C. This procedure left the samples with a moisture content such that after settling, a column of water from an eighth to a quarter of an inch deep appeared above the soil. This condition was considered much more comparable for the different soil classes than the method of adding a given volume of water to a definite weight of soil.

The tubes were taken from the chamber every week or ten days during the period of the experiment, the stoppers removed and the contents thoroughly stirred to allow the escape of any gases which might have formed.

Freezing point determinations were made immediately after the samples were washed and placed in the tubes and at frequent intervals thereafter. The freezing point depressions for representative samples are presented in table 1.

The data show that the virgin soils possess the power of giving up soluble material at a greater rate than the corresponding cropped soils. The divergence between the cropped and virgin samples in this respect is quite variable as would be expected since the degree of depletion in the different soils is quite different.

In most cases the greatest concentration obtained was considerably higher in the case of the virgin than of the cropped samples.

The tendency exhibited principally by the heavier soils to reach a maximum concentration of solution after 20-40 days and then decrease is undoubtedly due in part at least to the action of anaerobic organisms. It also seems highly probable that as hydrolysis and solution proceeded, changes may have occurred which resulted in precipitation of some of the dissolved salts. The possibility of adsorption should also be considered.

SOLUBILITY OF SUBSOILS FROM CROPPED AND VIRGIN AREAS

The finding of such a decrease in rate of solubility of surface soils as a result of continuous cropping at once suggests the question as to what effect depletion has on the solubility of the lower stratum or subsoil. To gain some information on this point a few subsoils were washed free of soluble salts, placed in freezing point tubes and maintained at 25°C. as outlined above. The freezing point depressions found at different times during the period of the experiment are shown in table 2.

It is surprising to note that these data show no appreciable difference in the rate of solubility of the subsoils from the depleted and virgin soils. In fact the solubility of all the samples is very slight. This agrees with the results of McCool and Millar (4) who determined the rate of solubility of subsoils collected from regions of great diversity of climatic conditions and found with few exceptions, a very low rate of solution.

TABLE 2
Rate of solution of virgin and cropped subsoils expressed as freezing point depressions

SOIL CLASS	CONDITION	DAYS MAINTAINED AT 25°C.					
		0	1	5	20	40	60
		°C.	°C.	°C.	°C.	°C.	°C.
Very fine sandy loam	Cropped	0.000	0.001	0.002	0.002	0.002	0.000
	Virgin	0.000	0.002	0.003	0.002	0.002	0.000
Sandy loam	Cropped	0.000	0.000	0.004	0.006	0.009	0.006
	Virgin	0.000	0.003	0.008	0.012	0.010	0.007
Silt loam	Cropped	0.000	0.001	0.003	0.001	0.002	0.000
	Virgin	0.000	0.004	0.006	0.002	0.003	0.004
Silt loam	Cropped	0.000	0.000	0.004	0.007	0.006	0.007
	Virgin	0.000	0.000	0.013	0.020	0.021	0.018

RELATIVE ABILITY OF CROPPED AND VIRGIN SOILS TO RENEW THE CONCENTRATION OF THE SOLUTION AFTER REMOVAL OF SOLUBLE SALTS BY WASHING

Bouyoucos (1) found that soils maintained at 53°C. had a more rapid rate of solubility than at room temperature. A preliminary experiment by the writer showed that soils washed free of soluble salts and then maintained at 50°C. with a moisture content slightly above saturation develop a rather high concentration of solution after forty hours. The virgin samples also showed a greater concentration than the corresponding cropped soils. It was deemed proper, therefore, to use this temperature and period of contact in the present experiment.

The soils were washed free of soluble salts on filters as previously described, then thoroughly mixed and quite large samples placed in freezing tubes. The tubes were stoppered and placed in the oven at 50°C. for forty hours, after which the freezing point depressions were determined and the soil again washed free of salts on small porcelain filters. The samples were made up to the proper moisture content and again placed in the oven for forty hours. This procedure was repeated several times. The data are presented in table 4.

TABLE 4

Relative ability of cropped and virgin soils to give up soluble material after successive washings to remove soluble salts shown by freezing point depressions

SOIL	CONDITION	FIRST PERIOD	SECOND PERIOD	THIRD PERIOD	FOURTH PERIOD	FIFTH PERIOD
		°C.	°C.	°C.	°C.	°C.
Fine sandy loam	Cropped	0.011	0.008	0.010	0.008	0.007
	Virgin	0.032	0.016	0.020	0.016	0.027
Silt loam	Cropped	0.011	0.002	0.008	0.004	0.007
	Virgin	0.028	0.019	0.025	0.020	0.017
Sandy loam	Cropped	0.025	0.013	0.013	0.013	
	Virgin	0.030	0.014	0.021	0.025	
Loamy sand	Cropped	0.019	0.001	0.004	0.002	0.001
	Virgin	0.044	0.021	0.022	0.018	0.020
Sandy loam	Cropped	0.014	0.003	0.002	0.003	0.005
	Virgin	0.027	0.011	0.011	0.008	0.013
Silt loam	Cropped	0.025	0.008	0.008	0.006	0.013
	Virgin	0.038	0.018	0.016	0.014	0.018
Loamy sand	Cropped	0.007	0.001	0.000	0.001	0.002
	Virgin	0.030	0.013	0.012	0.010	0.015

The results show that after the material going into solution during the first period is removed the depleted soils show only a feeble power to give up salts. It is interesting to note, however, that the concentration produced at each successive incubation is practically the same. This is in accord with the general observation that a soil will decline to a certain state of depletion and then continue to produce about the same yield from year to year. The productivity may, therefore, be taken as a measure of the rate of weathering of the less readily attacked minerals or the rate at which they give up soluble salts.

The virgin samples also show a decreased ability to give up soluble salts after the removal of the material liberated during the first period of incubation. Like the depleted sample the solutions also attain approximately the

same concentration at each succeeding incubation. The striking fact is that the concentration reached each time is much higher than is that of the corresponding depleted sample. This fact would lead one to predict the difference in productivity which exists.

EFFECT OF REMOVAL OF ORGANIC MATTER BY OXIDATION WITH HYDROGEN PEROXIDE ON SOLUBILITY OF CROPPED AND VIRGIN SOILS

Peterson (7) found that oxidation of the organic matter of surface soils with hydrogen peroxide resulted in an increased amount of phosphorus, iron, and aluminum soluble in 0.2 *N* HNO_3 but not of calcium or manganese. Treatment of subsoils showed no increase in the solubility of phosphorus. His conclusion was that phosphorus, iron, and aluminum are held in organic complexes and that the mineral particles of the soil are not affected by the oxidation process. It was decided, therefore, to determine the effect of removal of the organic matter by this method on the rate of solubility in water of the soils under consideration.

The procedure followed was to place 60 gm. of soil in an Erlenmeyer flask and add sufficient 3 per cent chemically pure peroxide to cover the soil. The contents of the flasks were thoroughly agitated every few hours and when the action had ceased enough 30 per cent peroxide was added to restore the liquid to approximately 3 per cent strength. When no further reaction was visible at room temperature the flasks were placed in a water bath at 30°C. and the above procedure repeated until practically all the organic matter was destroyed. The soils were now washed on filters with distilled water to free them of soluble materials after which they were thoroughly mixed and samples placed in freezing point tubes. These samples were maintained at 30°C. and freezing point determinations made after periods of 3, 7, 21 and 35 days. As controls, samples of the soils were given the same treatment as just outlined excepting that the peroxide was omitted. The data are found in table 5.

These results are very significant. In no case does the soil from which the organic matter has been removed show a lower rate of solubility than the corresponding untreated sample. On the other hand three of the soils show a distinctly higher rate of solubility and others a tendency for greater solubility when the organic matter is removed. This would seem to indicate that the organic matter, in place of being either the source of soluble material or the liberating agent, in reality retards the liberation of soluble salts. This seems plausible since the so-called humus is known to form a coating around the mineral particles and this may act as a protecting agent. In fact microscopical examination of some of the soils before and after treatment with peroxide showed the mineral particles to be much lighter colored in the treated samples. It must be recognized, however, that the soluble salts given up before removal of the organic matter may come largely from the organic material while after the removal of the organic coating fresh surfaces of the

mineral particles are exposed which have an even greater rate of solution. This is comparable to the finding of a decreased lime requirement of soils as the result of grinding.

The difference in rate of solubility between the cropped and virgin samples from which the organic matter had been removed was generally greater after the removal of the organic matter than before. This is very interesting inasmuch as it discredits the view occasionally expressed that soil depletion consists primarily in the loss of the major portion of the organic matter.

TABLE 5

Effect of removal of organic matter by H_2O_2 on the rate of solution of cropped and virgin soils shown by freezing point depressions

SOILS	CONDITION	DAYS MAINTAINED AT 30°C.									
		0		3		7		21		35	
		Normal	Treated	Normal	Treated	Normal	Treated	Normal	Treated	Normal	Treated
		°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Sandy loam	Cropped	0.000	0.000	0.000	0.005	0.004	0.017	0.005	0.035	0.014	0.034
	Virgin	0.000	0.008	0.005	0.006	0.007	0.023	0.030	0.031	0.029	0.031
Silt loam	Cropped	0.000	0.000	0.018	0.017	0.022	0.028	0.044	0.044	0.043	0.041
	Virgin	0.002	0.000	0.020	0.018	0.026	0.057	0.049	0.075	0.038	0.070
Fine sandy loam	Cropped	0.003	0.010	0.018	0.020	0.019	0.018	0.034	0.038	0.037	0.042
	Virgin	0.005	0.000	0.018	0.024	0.022	0.061	0.046	0.056	0.040	0.050
Loamy sand	Cropped	0.000	0.000	0.000	0.009	0.003	0.009	0.017	0.019	0.018	0.019
	Virgin	0.000	0.003	0.010	0.018	0.012	0.019	0.024	0.025	0.025	0.030

COMPOSITION OF MATERIAL GOING INTO SOLUTION FROM CROPPED AND VIRGIN SOILS

The next point of interest is to determine the differences in chemical composition of the soluble material going into solution from cropped and virgin soils.

The procedure followed was to place 2000 gm. of air dry soil in an aspirator bottle and stopper with a one-hole rubber stopper over which a small pad of glass wool was placed as a filter. The bottle was then inverted and water added through the tubulation and allowed to percolate through the soil until most of the soluble salts were removed. The hole in the rubber stopper was then closed and enough water added to slightly more than cover the soil. After standing at room temperature for three weeks the plug was removed from the stopper and the solution allowed to drain out. The soil was then washed by adding successive portions of distilled water and allowing it to percolate through. Solution and washings were thoroughly mixed

and aliquots used for analysis. The results in terms of parts per million of air dry soil appear in table 6.

These data bring out some interesting points. With one exception the depleted soils show a decidedly higher content of soluble sulfates. This is doubtless the result of the application of farmyard manure at various times during the period of cultivation. It would indicate that on these soils at least sulfur has not as yet become a limiting element in plant growth.

The results for chlorine are somewhat more variable as four of the soils show larger quantities in the virgin samples, two in the cropped samples

TABLE 6

Material going into solution from cropped and virgin soils upon standing 21 days at room temperature with high water content

SOIL	CONDITION	Ca(HCO ₃) ₂	Cl	Fe ₂ O ₃ + Al ₂ O ₃	Ca	Mg	SO ₄	P
		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Sandy loam	Cropped	109.35	12.59	2.95	6.75	2.21	13.66	1.08
	Virgin	341.70	18.89	8.02	17.75	6.75	5.03	0.80
Very fine sandy loam	Cropped	396.39	37.79	2.95	26.35	6.84	11.08	0.77
	Virgin	410.05	31.49	6.33	22.75	7.14	0.47	0.74
Silt loam	Cropped	177.65	6.30	18.14	11.00	3.23	12.67	0.71
	Virgin	628.75	6.30	30.80	43.00	7.30	6.08	0.74
Silt loam	Cropped	82.00	6.30	1.69	5.25	2.43	10.92	2.48
	Virgin	369.05	9.44	16.45	21.25	8.97	1.39	0.80
Loamy sand	Cropped	4.35	7.20	2.70	29.25	7.51	10.48	0.30
	Virgin	16.40	12.22	7.50	89.72	19.91	7.02	0.42
Sandy loam	Cropped	5.19	24.49	3.60	34.45	9.54	6.72	0.35
	Virgin	9.11	9.79	33.30	67.29	12.53	7.38	0.56
Loamy sand	Cropped	2.23	9.79	2.40	14.10	5.38	12.27	0.35
	Virgin	8.91	26.95	4.55	48.72	14.39	9.48	0.69

* Parts per million based on air dry soil.

and no difference in the other case. The amount of soluble phosphorus is also so variable that it cannot be stated that a decrease in amount of water soluble phosphorus results from many years of cropping.

Of the remaining determinations including alkalinity, iron and aluminum, calcium and magnesium the results without exception show larger quantities going into solution from the virgin soils. The decrease in soluble alkaline earths might be predicted as a result of increased leaching due to cultivation. The decrease in soluble iron and aluminum, however, was scarcely to be expected inasmuch as it has been shown that an increase in soil acidity is often accompanied by an increase in solubility of these elements.

RELATION OF THE RESPONSE OF SOILS TO FERTILIZER TREATMENT WITH
THE AMOUNTS OF NUTRIENTS IN THE SOIL SOLUTION

Inasmuch as the variations in the composition of the solutions from depleted and virgin soils were not as great as might be expected it was decided to determine if any relation exists between the response to an application of any element or combination of elements and the amounts of such constituents in the soil solution.

Two methods of obtaining the soil solution were employed. The first was by displacement with alcohol as described by Parker (6). The second procedure consisted in allowing the soils to stand eighteen days at room temperature with water in the ratio of one part of air dry soil to three parts of water. The containers were thoroughly shaken every day. The clear solution was obtained by filtering with a Büchner funnel.

The filtrates were analyzed for phosphorus, potassium, calcium, and magnesium and the results calculated to parts per million of air dry soil. The data appear in table 10 together with the greenhouse results.

In the case of the mineral soils it is seen that the soils which yielded the most calcium and magnesium by either method of extraction gave negative or very small returns as the result of treatment with calcium carbonate.

The amounts of phosphorus in the soil solution obtained by both methods were quite small but show some correlation with the increase of plant growth due to addition of this element. The correlations are better when the results from the dilution method are considered.

The data for potash show little correlation when the results from the displacement method are considered. When the dilution method was used, however, the amounts of the element extracted correlate rather closely with the response of alfalfa to addition of potassium. Soil 127 is something of an exception to this but it should be noted that this soil was productive without fertilizer treatment. The decreased growth resulting from additions of potassium alone in the case of two of the sands is doubtless due to an increase of active acidity as a result of the addition of the potassium salt.

In the case of the peat soils the results from neither method of extraction correlate well with the response in plant growth due to addition of the plant food elements.

Inasmuch as the data just presented show that the dilution method indicates the need of the soil for plant food elements much better than the displacement method it was considered probable that a method involving a larger proportion of water to soil and a shorter period of contact would be still more satisfactory. Accordingly samples were prepared using five parts of water to one of soil in the case of mineral soils, and seven and one-half of water to one of soil for the peats. The samples were allowed to stand twenty hours at room temperature and then filtered. The results of the determinations on the filtrate are found in table 11.

TABLE 10
Relation of mineral elements in the soil solution to response of soils to fertilizer treatments

SOIL		CONSTITUENTS OF SOIL SOLUTION										WEIGHT OF DRY ALFALFA (3 CROPS)					
Class	Number	Displacement method					Dilution method					Total weight of check	Increase due to addition of				
		Ca	Mg	P	K	p.p.m.	Ca	Mg	P	K	p.p.m.		K	P	P + K	CaCO ₃	K + P + (CaCO ₃)
Silt loams.....	253	112.0	48.4	5.6	2.5	p.p.m.	180.0	89.0	5.0	3.4	p.p.m.	36.00	11.95	-6.25	21.98	-4.52	24.03
	127	31.3	8.5	5.0	6.2	p.p.m.	129.0	40.3	6.6	10.9	p.p.m.	57.72	5.43	2.73	9.78	7.68	14.75
	141	43.9	10.5	4.7	5.4	p.p.m.	97.0	20.1	4.1	8.0	p.p.m.	20.80	2.20	12.15	18.53	3.10	27.95
	225	65.1	33.2	6.1	3.2	p.p.m.	172.0	84.3	4.5	7.7	p.p.m.	46.73	3.77	2.77	24.79	-6.58	22.07
	239	29.3	11.2	4.3	2.9	p.p.m.	41.5	17.7	2.7	2.5	p.p.m.	19.93	10.47	10.92	25.72	4.20	25.80
Fine sandy loam.....	71	39.4	10.4	7.3	19.5	p.p.m.	67.0	26.4	19.6	8.9	p.p.m.	51.15	3.25	5.35	0.07	4.35	10.10
Sands.....	85	29.3	3.4	2.1	2.6	p.p.m.	50.0	17.4	14.7	6.6	p.p.m.	60.77	1.68	0.68	1.10	-0.72	0.90
	296	10.0	3.9	3.0	1.4	p.p.m.	15.0	12.1	2.9	6.4	p.p.m.	30.05	-4.50	7.35	10.17	4.60	17.65
	281	7.0	2.6	1.2	2.3	p.p.m.	29.0	2.9	6.8	4.2	p.p.m.	22.75	-4.40	7.05	15.35	17.17	31.17
Peats.....	337	442.7	238.4	26.7	41.0	p.p.m.	1056.0	471.9	50.0	61.5	p.p.m.	52.49	2.06	11.51	35.31	-5.59	32.31
	309	82.3	54.9	20.8	15.3	p.p.m.	66.0	56.6	30.0	17.3	p.p.m.	38.12	1.68	3.58	17.60	2.38	22.98
	267	76.8	27.3	18.8	35.3	p.p.m.	102.0	48.3	35.7	52.8	p.p.m.	28.48	5.32	14.57	16.82	21.27	42.55

TABLE II
Relation of mineral elements extracted from soils by water to response to fertilizer treatments

SOIL	Num- ber	SOIL SOLUTION				ACIDITY OF SOIL	TOTAL P CONTENT	WEIGHT OF 3 CROPS OF ALFALFA	HISTORY OF SOILS
		Cu	P	K					
Class		p.p.m.	p.p.m.	p.p.m.			per cent	gm.	
Silt loam.....	253	180.0	14.2	11.6		Not acid	0.10	36.00	Cropped 1 year. Crops poor
	127	72.5	24.3	26.6		Medium	0.054	57.72	Virgin soil. Good volunteer clover
	141	55.0	15.3	10.1		Strong	0.047	20.80	Cropped 20 years—has received considerable manure— yields decreasing
	225	112.5	16.0	6.4		Very slight	0.090	46.73	Crops good on this part of field
Fine sandy loam....	239	42.5	5.3	9.8		Strong	0.066	19.93	Same field as 225—crops do poorly on this part of field and legumes fail
	71	45.0	21.4	25.6		Medium		51.15	Virgin. Good volunteer clover
Sands.....	85	85.0	16.0	18.3		Slight	0.042	60.77	Virgin. Good growth of clover
	296	27.5	5.1	8.7		Medium	0.023	30.05	Cropped 20 years—has received little manure— legumes fail
	281	30.0	5.8	9.8		Medium	0.023	22.75	No history available
	337	145.3*	13.4	16.8		Not acid	0.085	52.49	Grew 100 bushels of corn after being manured and fertilized—cropped 1 year
Peats.....	309	31.9	2.8	8.7		Strong	0.11	38.12	Cropped 3 years—had 1 ton of lime and some ferti- lizer—crops fair
	267	16.8	6.0	15.2		Very strong	0.141	28.48	In blue joint grass 30 years

* Data for peats have been divided by four to correct for difference in volume weight between peats and mineral soils.

These results show some rather remarkable correlations. Considering first the silt loams it is seen that whenever a large amount of calcium is extracted the yields of alfalfa are large even though the amounts of phosphorus and potassium in the soil solution are small. On the other hand when the amount of calcium going into solution is not unusually large but the concentrations of phosphorus and potassium are high the yield is also quite large. This is exemplified by soil 127.

It is also of interest to note that the amounts of calcium dissolved by this method correlate more closely with the acidity as determined by the Truog method than do the amounts of calcium found in the soil solution by the displacement method. It is noteworthy that the amounts of phosphorus extracted by this method do not correlate with the total phosphorus present.

The sandy soils exhibit the same characteristics noted above. Number 85 showed a high solubility of calcium, phosphorus and potassium and produced a large yield of alfalfa while the other two sands showed a mediocre solubility of these elements and also indifferent growth of alfalfa.

In the case of the peat soils number 337 is outstanding in the amount of the three plant food elements going into solution and also in the yield of alfalfa. Soil 309 has a low solubility of phosphorus and potassium but a comparatively high solubility of calcium and shows a medium growth of crop. Soil 267 shows a considerably higher solubility of phosphorus and potassium than soil 309 but a much lower solubility of calcium and also a somewhat less growth of alfalfa.

The results for the soils as a whole are extremely interesting. In several instances they lend support to the explanation of the difference in feeding power of plants given by Truog (11) to the effect that alfalfa may feed readily on a low concentration of phosphorus and potassium if sufficient lime is present. In cases where the amount of lime is limited a higher concentration of the other elements is necessary for satisfactory growth.

A point strongly emphasized by the greenhouse tests is that in interpreting the results of greenhouse or plat tests the data from all the treatments must be considered in order to determine whether or not a soil is in need of any particular element or treatment. This is well illustrated by soil number 253. When phosphorus alone was applied to this soil the yield was decreased but when phosphorus and potassium were both used the increase was almost double that obtained when potassium was applied alone. Calcium carbonate also decreased the yield when used alone but in conjunction with phosphorus and potassium the growth of alfalfa was greater than on the pot receiving a combination of phosphorus and potassium without lime.

Soil 309 lends support to the points brought out above. The increased yield from an application of both phosphorus and potassium is much greater than one would be led to expect from the increase noted when these elements were applied singly. The increased growth of alfalfa on the pot receiving phosphorus, potassium and lime was also somewhat greater than might be

anticipated from the meager increase due to lime alone and the combined effects of phosphorus and potassium.

More exact conclusions regarding the needs of these soils could have been drawn had the treatment included combinations of phosphorus and lime and potassium and lime. Under those conditions the need of or response to phosphorus could be determined by comparing the results from the potassium lime treatment with the phosphorus, potassium lime treatment. Similarly the effects of potassium could be determined by comparison of results from the phosphorus lime treatment with those from the potassium phosphorus lime treatment.

The interpretation of the results of the tests is somewhat complicated by the fact that disodium phosphate was used as a source of phosphorus. Inasmuch as this salt may decrease acidity somewhat the results from its application may be due in part to this factor as well as to the addition of phosphorus.

Considering all the data from the various methods of extraction employed and the solubility measurements made by the freezing point method, it appears that the rate of solution of calcium and other plant food elements is in reality the important factor rather than the total amounts in the soil solution at any given time.

SUMMARY

A study of forty-eight depleted and the corresponding virgin soils showed the latter to have a greater rate of solubility, as measured by the freezing point method, when maintained at 25°C. with a moisture content somewhat above saturation. The fact that a considerable number of soils were studied and rather uniform results were secured would seem to warrant a rather general conclusion that a decrease in rate of solubility is one of the important changes a soil undergoes in passing from a virgin to a more or less depleted condition.

An equal or greater rate of solution was observed in several soils after removal of the organic matter by treatment with hydrogen peroxide than in the untreated samples. The difference in rate of solubility between cropped and virgin soils from which the organic matter had been removed by means of hydrogen peroxide was generally greater than in the untreated samples. These results lead to the conclusion that the larger supply of organic matter generally present in virgin soils may not necessarily be the cause of their greater rate of solubility.

The solubility of a number of subsoils was found to be very low compared to the surface soils. It was also found that subsoils from depleted areas had as great a solubility as subsoils from the corresponding virgin soils. This leads to the conclusion that most crop plants feed primarily in the surface or plowed stratum of the soil.

The amounts of various materials going into solution from depleted and virgin soils maintained for three weeks at room temperature with a moisture

content somewhat above saturation were determined. With one exception, the cropped soils yielded more sulfates while the virgin soils gave the larger amounts of iron, aluminum, calcium, and magnesium. Phosphates and chlorides were given up in larger quantities by the virgin soils in some cases and by the cropped soils in other cases.

Comparisons were made of the yields of alfalfa on untreated soils and soils receiving applications of calcium carbonate and various plant food elements alone and in combination with the amounts of various nutrients in the soil solution obtained by three different methods.

When the displacement method was used a fair correlation was noted between the amounts of calcium and phosphorus in the soil solution from several silt loams and the response of plant growth to addition of these elements. The data for the sandy soils used do not show such a good correlation and little or no correlation was found in the case of several peat soils. The amounts of potassium in the solutions showed little relation to the response of plant growth to addition of potassium in any of the soil classes.

When the soils were extracted with three parts of water to one of soil by weight with a period of contact of eighteen days fair correlations were observed in so far as phosphorus and calcium are concerned in both the silt loam and sandy classes. Also more consistent relations with respect to potassium were found than when the displacement method was used. The results for the peat soils showed practically no correlation.

The total amounts of material found in the extracts agree quite well with the growth of alfalfa produced on the check pots.

When the soils remained in contact with larger proportions of water (one to five for the mineral soils and one to seven and one-half for the peats) for twenty hours, the total amounts of material extracted show a very remarkable correlation with the yields of alfalfa produced on the untreated soil.

In cases where comparatively large amounts of calcium went into solution but only small quantities of phosphorus and potassium the growth of alfalfa was quite satisfactory, thus indicating that a highly available lime supply may render adequate small amounts of these elements.

The data as a whole indicate that the rate at which various materials are given up by soils is a very important factor in determining their crop producing capacity. Studies along this line are being extended.

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RECIPROCAL REPRESSION EXERTED BY CALCIC AND MAGNESIC ADDITIONS UPON THE SOLUBILITY OF NATIVE MATERIALS IN SURFACE SOIL

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INTRODUCTORY

In a previous contribution (10) it was shown that basic interchange was brought about in the *subsoil* by surface-soil leachings impregnated with a preponderance of either calcium or magnesium. It was also shown that an excess of solid phases of one base was *depressive* upon the *surface-soil* outgo of the other. In the earlier work, which extended over an 8-year period, seven calcic and magnesian materials were applied in excessive amounts. Each material was added in chemical equivalence at three rates, 8, 32, and 100 tons of CaO per 2,000,000 pounds of soil. The present contribution is the result of a 5-year lysimeter study with another, though similar, soil to which light additions of limestone, dolomite, CaO, and MgO were made. Both light and heavy amounts of CaO and MgO were used also in conjunction with each of three sulfur carriers, FeSO₄, pyrite, and elementary sulfur. The 8-year study was based upon an installation of both shallow and deep tanks, and certain functions of the subsoil were definitely determined. In the study here reported, however, the lysimeters contained surface soil only. In previous reports the outgo of sulfates (7) and the depressive activities of the calcic and magnesian additions upon potassium outgo (8) were reported for the same tanks. Nitrates and bicarbonates have also been determined, though not reported. This article deals with the total leachings of salts of calcium and magnesium, as such are influenced by form and amount of addition, basic repression, and both initially soluble sulfate and sulfate generated by chemical oxidation and sulfonation of the two unoxidized forms of sulfur. In the interpretation of the calcium and magnesium outgo from those tanks which received the supplements of sulfur carriers it is helpful to have available the data as to their sulfate leachings (7).

METHODS

As stated in the paper (7) on sulfate outgo, the 3750-pound addition was intended to represent a 2000-pound application of burnt lime plus 1750 pounds to care for the immediate or potential acidity of the sulfurous materials. Limestone and dolomite additions were both of 100-mesh fineness. The acid loam used contained 0.217 per cent of CaO and 0.398 per cent of MgO, as determined by Na₂O₂-Na₂CO₃ fusion. Descriptions of equipment used, analyses of treatments, and precautions followed in handling and mixing treatments throughout the body of the soil have been given, (4, 7) and will not be repeated here. The amounts of calcium and magnesium brought down in rainfall also have been reported (5), but these experimental and minor constants will be considered as inherent in the soil.

PRESENTATION AND DISCUSSION OF DATA

Annual losses of calcium, totals for the five years, and average annual increases or decreases above the control are shown for the twenty-two tanks in table 1. The magnesium data are given in similar form in table 2. Totals of calcium-magnesium salts from the control and light unsupplemented additions are presented in table 3. Since all treatments were based upon chemical equivalence, the results are reported throughout in terms of CaCO_3 . The discussion of results follows the order of treatment and grouping of tables 1, 2, and 3.

TABLE 1

Annual and total amounts of calcium salts leached from "Cherokee" loam during a 5-year period—treatments of limestone, and dolomite, and of CaO and MgO with and without additions of FeSO_4 , pyrite and powdered sulfur

TANK NUMBER	TREATMENT			CaCO ₃ EQUIVALENT PER 2,000,000 LBS. OF SOIL								
	Calcic-Magnesian		Sulfur constant of 1,000 lbs. per 2,000,000 lbs. of soil	Annual periods					5-year period			
	Material	CaO equivalent per 2,000,000 lbs. of soil		First	Second	Third	Fourth	Fifth	Average annual	Total	Increase over no-treatment control	
		<i>lbs. or tons</i>		<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	<i>lbs.</i>	
50	None	None	None	291	248	234	260	188	244	1,221	
51	Limestone	2000	None	370	406	336	351	201	333	1,664	443	
52	Dolomite	2000	None	230	273	228	219	166	223	1,116	-105	
53	CaO	2000	None	406	408	278	371	226	340	1,689	468	
54	CaO	3750	None	694	587	477	482	293	507	2,533	1,312	
55	MgO	2000	None	155	147	166	161	111	148	740	-480	
56	MgO	3750	None	147	143	166	160	96	142	712	-509	
57	None	None	FeSO ₄	1,348	611	374	278	173	557	2,784	1,563	
58	CaO	3750	FeSO ₄	2,536	718	351	338	205	830	4,148	2,927	
59	MgO	3750	FeSO ₄	579	139	121	101	89	206	1,029	-192	
60	CaO	32 tons	FeSO ₄	3,799	1,648	1,863	1,350	1,229	1,980	9,889	8,668	
61	MgO	32 tons	FeSO ₄	82	60	103	94	60	80	399	-822	
62	None	None	Pyrite	585	896	615	381	308	557	2,785	1,564	
63	CaO	3750	Pyrite	865	1,108	643	869	380	773	3,865	2,644	
64	MgO	3750	Pyrite	297	242	166	159	48	182	912	-309	
65	CaO	32 tons	Pyrite	4,950	1,724	1,276	1,496	1,161	2,121	10,607	9,386	
66	MgO	32 tons	Pyrite	99	69	88	92	56	81	404	-817	
67	None	None	Sulfur	1,279	617	400	306	186	558	2,788	1,567	
68	CaO	3750	Sulfur	2,311	903	384	344	234	835	4,176	2,955	
69	MgO	3750	Sulfur	526	209	245	189	119	258	1,288	67	
70	CaO	32 tons	Sulfur	4,162	1,968	1,772	1,864	1,342	2,222	11,108	9,887	
71	MgO	32 tons	Sulfur	55	65	90	104	59	75	373	-848	
Rainfall (August to August) in inches.....				37.69	51.54	54.75	55.19	56.75	51.16	

TABLE 2

Annual and total amounts of magnesium salts leached from "Cherokee" loam during a 5-year period—treatments of limestone, and dolomite, and of CaO and MgO with and without additions of FeSO₄, pyrite and powdered sulfur

TANK NUMBER	TREATMENT			CaCO ₃ EQUIVALENT PER 2,000,000 LBS. OF SOIL								
	Calci-Magnesic		Sulfur constant of 1,000 lbs. per 2,000,000 lbs. of soil	Annual periods					5-year period			
	Material	CaO equivalent per 2,000,000 lbs. of soil		First	Second	Third	Fourth	Fifth	Average annual	Total	Increase over no-treatment control	
50	None	None	None	174	90	108	78	85	107	535	
51	Limestone	2000	None	143	72	59	209	60	109	543	8	
52	Dolomite	2000	None	338	226	150	230	169	223	1,113	578	
53	CaO	2000	None	159	82	61	100	75	95	477	—58	
54	CaO	3750	None	139	67	42	162	74	97	484	—51	
55	MgO	2000	None	555	329	288	335	112	324	1,619	1,084	
56	MgO	3750	None	980	556	514	527	263	568	2,840	2,305	
57	None	None	FeSO ₄	474	140	106	147	62	186	929	394	
58	CaO	3750	FeSO ₄	347	96	55	113	83	139	694	159	
59	MgO	3750	FeSO ₄	3,683	534	349	348	227	1,028	5,141	4,608	
60	CaO	32 tons	FeSO ₄	100	9	33	76	57	55	275	—260	
61	MgO	32 tons	FeSO ₄	3,619	5,770	4,074	3,566	1,885	3,783	18,914	18,379	
62	None	None	Pyrite	300	202	142	184	129	191	957	422	
63	CaO	3750	Pyrite	373	119	68	118	85	153	763	228	
64	MgO	3750	Pyrite	1,140	1,033	546	518	291	706	3,528	2,993	
65	CaO	32 tons	Pyrite	96	48	17	87	28	55	276	—259	
66	MgO	32 tons	Pyrite	5,474	6,370	5,015	3,277	1,877	4,403	22,013	21,478	
67	None	None	Sulfur	523	151	112	132	82	200	1,000	465	
68	CaO	3750	Sulfur	280	99	57	112	40	118	588	53	
69	MgO	3750	Sulfur	3,340	795	340	769	213	1,091	5,457	4,922	
70	CaO	32 tons	Sulfur	86	35	26	62	45	51	254	—281	
71	MgO	32 tons	Sulfur	4,917	7,169	5,187	3,010	1,785	4,414	22,068	21,533	
Rainfall (August to August) in inches.....				37.69	51.54	54.75	55.19	56.75	51.16	

CALCIUM LEACHINGS FROM TWENTY-TWO TANKS

Limestone-dolomite-oxide group

The limestone addition increased the outgo of calcium for each of the five years. The 5-year total amounted to 443 pounds, or an annual average increase of 89 pounds. On the other hand, the equivalent dolomite addition

depressed the outgo of calcium below that of the control during four of the five years, the total depression amounting to 105 pounds.

Both CaO additions increased calcium concentrations in the leachings. The 1750-pound supplement to the 2000-pound addition augmented, by 844 pounds for the five years, the 468-pound increase caused by the 2000-pound addition. From previous studies with practically the same soil (3), it was determined that an application of 4000 pounds of CaO was all fixed in non-hydrate and non-carbonate forms within less than ten days. The increase in calcium leachings came, therefore, from the solvent action of acids formed biologically and by increase in bicarbonates derived through hydrolysis of the calcium silicates.

The decreased yields of calcium from the two magnesia additions were in close agreement, with striking uniformity for annual losses. The carbonate elimination, through fixation, observed with reference to CaO was known to

TABLE 3
Five-year totals of calcium-magnesium outgo from 2000-pound CaO-equivalent additions of CaO, MgO, limestone and dolomite and 3750-pound CaO and its MgO equivalent

SALTS LEACHED	LOSSES EXPRESSED AS CaCO_3 -EQUIVALENT PER 2,000,000 POUNDS OF SOIL						
	Control	From treatments (equivalent to 2,000 lbs. CaO) of:				From 3,750-lb. CaO-equivalent treatments of:	
		CaO	MgO	Lime- stone	Dolo- mite	CaO	MgO
		lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Calcium.....	1,221	1,689	740	1,664	1,116	2,533	712
Magnesium.....	535	477	1,619	543	1,113	484	2,840
Total.....	1,756	2,166	2,359	2,207	2,229	3,017	3,552
Combined Ca-Mg increases in excess of outgo from control...	410	603	451	473	1,261	1,796

have taken place also in the case of MgO. The positive depressions of 480 pounds and 509 pounds below the calcium outgo from the control are in harmony with the similar findings (10) where the same repressive effect was exerted by excessive and unabsorbed amounts of MgO, and also MgCO_3 and magnesite. Still further proof of the action of both light and excessive additions will be offered in this paper in the discussion of the sulfur-supplemented MgO additions, which have continued to show the depressive effect through all five years. It will be noted that the average outgo from the two MgO tanks during the fifth year was only 55 per cent of that from the control.

FeSO_4 -oxide group

The action of FeSO_4 upon native alkali-earths was apparently direct. The increase in outgo of the sulfate radical from this treatment was attributable almost entirely to its combination with calcium and magnesium. Only a small

increase in potassium outgo resulted from the treatment, as has been shown in a previous contribution (8). Lipman (2) reported the calcium and potassium content of a pressure-extraction solution obtained from lemon orchard soil, which had been treated with 5-10 pounds of commercial FeSO_4 for each tree. The FeSO_4 treatment almost doubled the soluble calcium recoverable by this method of obtaining a soil solution. The 1563-pound increase in calcium outgo is four times the corresponding increase in magnesium leachings, though the native calcium content of the soil is only about one-half that of the native magnesium. From this it is evident that the calcium complexes are much more subject to the solvent derived from FeSO_4 than those of magnesium.

The 2000-pound supplement to the 1750-pound addition required to care in full for the sulfate radical was also drawn upon, most probably, to account for the still further increased outgo from tank 58. The 4148-pound total from this tank, 2536 pounds of which came out during the first year, is 2927 pounds in excess of the loss from the control and 1364 pounds more than the increased loss of native calcium from the unsupplemented FeSO_4 addition. The sudden drop from the maximum of the initial year, and the progressive decreases during the last four years, mark the removal of a major portion of the calcium sulfate and the advent of a large proportion of calcium bicarbonate. This outgo in calcium harmonizes with the periodicity of sulfate leachings which have been reported (7).

The calcium leachings from the 3750-pound MgO-FeSO_4 treatment during the first year amounted to more than one-half of the 5-year total. The influence of magnesium sulfate derived from the MgO-FeSO_4 additions is evidenced during this period. Most of the added sulfate having passed out during the first year, the residue of the magnesia addition exerted thereafter a depressive influence upon calcium outgo, which amounted to only 450 pounds, as against 930 pounds from the control for the last four years. The balance between the 288-pound increase of the first year and the 480-pound cumulative depression of the last four years amounted to 192 pounds. In other words, in spite of the magnesium-calcium interchange brought about by magnesium sulfate during the period before its removal by leaching, the magnesia addition still demonstrated a conservation of the native stores of calcium.

The greatest yield of calcium from the 32-ton CaO treatment used in conjunction with the ferrous sulfate came during the first year. With varying proportions this yield was accounted for by hydroxide, sulfate, nitrate, carbonate, and bicarbonate of calcium. After the first year the outgo decreased progressively. Of the total increase of 8668 pounds above the control for the 5-year period, an increase of 3508 pounds, or 40 per cent, is accredited to the first year. But this 40 per cent outgo of added CaO carried only 82.2 pounds of the 1000 pounds of sulfur added in the soluble sulfate form (7).

Applied with FeSO_4 , the 32-ton MgO addition gives a still more striking depressive influence upon calcium-salt outgo. The excess of MgO entirely nullified the liberative or replacement activity which was apparently exerted by

the magnesium sulfate derived from the lighter MgO addition with FeSO_4 . During each of the five years the calcium outgo was but a fractional part of that from the no-treatment control, and a still smaller fraction of that from the sulfate control. The 5-year total of 399 pounds from tank 61 falls 822 pounds short of equalling that from the no-treatment tank 50, and 2385 pounds below that of tank 57, the FeSO_4 control.

The pyrite-oxide group

The order of annual losses of calcium from the pyrite control differed from that of the FeSO_4 control. The unsupplemented pyrite increased the 291-pound loss from the no-treatment control to 585 pounds, during the first year, as against 1348 pounds for the sulfate control. The oxidation of the pyrite apparently was most extensive during the second year, as indicated by the maximum calcium yield, and also by the maximum sulfate leaching during that year (7). The total calcium increase caused by the pyrite during the 5-year period was practically identical, however, with that caused (7) by ferrous sulfate and by elementary sulfur, though the pyrite addition gave the minimum sulfate recovery of the three materials during that time. These three CaCO_3 -equivalent totals were, respectively, 1564, 1563, and 1567 pounds per 2,000,000 pounds of soil. But when added with pyrite, the light lime treatment enhanced the total calcium outgo by only 2644 pounds, or 293 pounds less than when used with ferrous sulfate and 311 pounds less than when used with elementary sulfur. This disparity is accounted for by the fact that the oxidation of the pyrite addition was less rapid and less in the aggregate than that of the elementary sulfur (7), for the sulfur recoveries from the FeSO_4 and elementary sulfur were both over 90 per cent of the additions, after deduction of the 5-year rainfall sulfur, while the pyrite gave a corresponding recovery of only 60 per cent.

When added with pyrite, the light MgO addition exhibited, after the second year, a depressive effect similar to that shown by the same oxide when used with ferrous sulfate. The largest leachings of both calcium and sulfates occurred during the first two years. Because the oxidation of pyrite was less rapid in the pyrite-MgO tank than in the pyrite control (7), less of magnesium sulfate was at hand to offset the depressive action of the MgO treatment. Hence, the depressive action of the light MgO addition was considerably greater when used with pyrite than when used with ferrous sulfate. It will be noted that after the 6-pound increase of the first year the treatment showed progressive annual depressions of 6, 68, 101, and 104 pounds below corresponding no-treatment yields.

The maximum outgo from the pyrite and 32-ton CaO addition came during the first year, with a tendency toward progressive decrease thereafter. During the early period, as parallel with persistence of the hydrate, the outgo of lime was almost entirely in forms other than sulfate, a total sulfate sulfur recovery of only 31.5 pounds having been obtained from the 1000-pound addition (7).

The excess of CaO was either depressive to both chemical oxidation and sulfonation, or inactive toward one or both of these processes, yet depressive upon sulfate removal by leaching, if sulfates were formed. For, as has been previously pointed out (7), not only was the excess of CaO depressive to the outgo of sulfates from pyrite, but during the persistence of hydrate it also inhibited the outgo of the added sulfate of iron, since only 82.2 pounds of the 1000-pound addition of sulfate sulfur was leached during the first year.

Applied with pyrite, the 32-ton MgO addition again proved distinctly depressive upon the outgo of native calcium during each of the five years. Even had MgSO_4 been present as a liberating salt, the excess of MgO was such as to nullify any tendency to effect basic exchange. This was shown in the case of the 32-ton MgO and FeSO_4 treatment. Differing, however, from the elementary sulfur and heavy MgO combinations, where the MgO proved accelerative to the formation of sulfates, the same addition of MgO exerted the opposite effect upon the pyrite. The total depression in calcium outgo amounted to 817 pounds. This is in remarkable agreement with the 5-year totals of 822 pounds and 848 pounds for the same oxide and rate when used in conjunction with ferrous sulfate and elementary sulfur, respectively.

Sulfur-oxide group

The sulfur addition increased the concentration of calcium salts in the leachings from the control during each of the first four years, particularly during the first year. Both calcium outgo and sulfate recoveries (7) progressively decreased during the 5-year period. Total outgo, as has been previously mentioned, is very close to losses from the other two sulfur-carrier controls.

The light CaO addition accelerated conversion of the elementary sulfur into sulfates, as was demonstrated by the increase in sulfate leachings (7). A large part of the 2020-pound increase over the calcium outgo from the untreated tank during the first year is accounted for in this way, since 733.5 pounds of sulfate sulfur came from the combination of light lime and sulfur during the first year, as against 506.8 pounds from the unsupplemented sulfur control. The rate of outgo of calcium decreased progressively during the five years. The same was true also of sulfate leachings. Of the total 3750-pound CaO addition, including the 1750-pound portion intended to care for potential acidity, 2955 pounds were leached. That is, the excess above the outgo from the control represented the 1750-pound neutralizing addition plus 1205 pounds, or 60 per cent, of the 2000 pounds intended as the soil-ameliorant treatment.

In agreement with the corresponding MgO addition in the ferrous sulfate group, the lighter MgO produced an increased outgo of calcium during the first year, during which period 816.6 pounds of sulfate sulfur (7) was removed by leaching. The calcium liberation was apparently caused by the activity of engendered magnesium sulfate. Depressive influence of MgO in the MgO-sulfur combination was evidenced after the third year, when the effect of the generated sulfate had been eliminated because of its removal. The liberation

of calcium by the engendered magnesium sulfate during the first year was more than sufficient to offset the depression in calcium outgo during the latter period. As a result, there was a gain of 67 pounds over the no-treatment control during the 5-year period. Comparing the yield from tank 69 with the findings from tanks 64 and 59, it appears that with intensive initial and progressively decreasing generations of magnesium sulfate the depressive action of MgO was nullified for the 5-year period; that with slower and more irregular oxidation of pyrite and a resultant minimum of magnesium sulfate occurrence, the most depressive influence exerted by the light MgO addition was of effect; and, with the maximum amount of magnesium sulfate formed and leached during the first year, the intermediate depressive activity was in evidence.

The maximum calcium outgo from the heavy CaO and sulfur addition came during the first year. Only a small part of this early outgo could be accounted for by the 88 pounds of added sulfur which was leached out in the sulfate combination. During the persistence of considerable quantities of $Ca(OH)_2$ from the CaO addition, sulfonation was most probably inhibited or greatly depressed. Even had sulfonation taken place, however, the $CaO-FeSO_4$ parallel demonstrated that sulfates so generated would not have been leached (7).

Incorporated in the soil along with sulfur, the heavy MgO addition again shows a result which corresponds to that obtained when it was used in conjunction with both ferrous sulfate and pyrite. It has been shown (7) that, when admixed with 32 tons of MgO , the elementary sulfur was rapidly converted into sulfates. But the resultant excess of magnesium sulfate induced no magnesium-calcium interchange when in contact with the large excess of unabsorbed MgO . This result is also in agreement with that obtained when the soluble sulfate was added along with the heavy addition of MgO . The uniformity of calcium outgo from the heavy treatment of MgO may be stressed by repetition of the comparison between tanks 71, 66, and 61. The disparities below the outgo from the no-treatment control demonstrated repressions in the solubility of native calcium, as represented by depressions in calcium outgo of 848, 817, and 822 pounds, respectively.

MAGNESIUM LEACHINGS FROM 22 TANKS

Limestone-dolomite-oxide group

The 100-mesh limestone depressed the outgo of magnesium during four of the five years. The accelerative influence indicated during the fourth year was sufficient, however, to offset the cumulative differences which resulted from the reverse action during the other four years. Many of the losses for the fourth year indicated that the periodicity of rainfall during that period caused abnormality in the leaching of soluble salts.

Magnesium outgo from the dolomite addition was consistently higher than from the control. As a result, the magnesium increase for the 5-year period was slightly more than 100 per cent of the loss from the no-treatment tank.

Again, as in the case of the limestone additions, the economic additions of CaO caused a decreased magnesium outgo during four of the five years; but the abnormality of the fourth year served to neutralize, in part, the cumulative results of the other four years. Hence, the two CaO treatments showed magnesium depression totals of but 58 pounds and 51 pounds.

Both MgO additions showed a substantial influence upon magnesium outgo. The 3750-pound treatment gave results consistently higher than those from the 2000-pound application. Were it not for the abnormality in leachings common to the six tanks 51-56 during the fourth year, both MgO additions would have shown maximum outgo during the first year, with progressive decreases during the succeeding four years. The increase from the 2000-pound addition was 54 per cent of the amount added, while that from 3750 pounds of MgO was 61 per cent of the addition.

FeSO₄-oxide group

The solvent action of the unsupplemented FeSO₄ treatment was most marked during the first year. Over one-half of the added sulfate was recovered during that period. The 394-pound gain in the magnesium leachings of the first year represented an increase of 73.6 per cent over the outgo from the no-treatment control.

The light CaO supplement to the FeSO₄ treatment caused the formation of CaSO₄, and this salt apparently effected an interchange with native magnesium. After the removal of the CaSO₄ and MgSO₄ so accounted for, the residual effect of the CaO was more repressive than augmentive. As a result of such direct solvent action and interchange, the supplemented ferrous sulfate induced a 5-year increase of only 159 pounds in magnesium outgo, as against 392 pounds where the FeSO₄ was not subjected to the intervening influence of the CaO supplement.

Of the total increase of 4608 pounds from the 3750-pound MgO addition with FeSO₄, 3509 pounds, or 73.6 per cent, was leached during the first year, after which period there was a tendency toward progressive decrease to the minimum outgo of the fifth year. The total outgo of 5141 pounds represented a gain of 4608 pounds, or 858 pounds more than the addition. Thus, from an addition of MgO in connection with FeSO₄, solvent action of the soluble salt plus biological activation has resulted in a large supplemental loss of the native magnesium.

The heavy addition of CaO exerted a decidedly depressive tendency upon the yield of native magnesium to the free soil water. The large excess of the oxide nullified the liberative tendency of 4246 pounds of calcium sulfate formed by reaction between Ca(OH)₂ and the soluble iron sulfate. The magnesium outgo was consequently decreased to about one-half of that from the no-treatment control. Contrasted with the enhanced outgo from the FeSO₄ control, this decreased outgo gives a differential of 654 pounds, as representing the extent of the repressive action of the excess of calcium oxide.

The 32-ton MgO addition was more than sufficient to saturate the soil by exceeding its capacity to absorb, or "silicate," the added oxide. A large excess of MgO was therefore available for carbonation and leaching as bicarbonate by direct reaction of available H_2CO_3 , whereas hydrolysis of the completely absorbed 3750-pound addition was essential to its removal in the bicarbonate form. Nitrate and sulfate generations were also accelerated by the heavy addition. As a result, an increased magnesium outgo of 18,379 pounds was obtained.

Pyrite-oxide group

Oxidation of the pyrite-control treatment was sufficiently rapid to cause an appreciable increase in outgo of magnesium for each of the five years. The total increase for the 5-year period was almost equal to the outgo from the control. After the maximum of the first year, the annual losses showed tendency toward progressive decrease.

Subsequent to the first year, there was little evidence of magnesium liberation from the light addition of CaO. Of the total increase of 228 pounds over the pyrite control, 199 pounds came during the first year, and should be considered most probably as a sequence of pyrite oxidation and either direct solvent action or interchange resulting from the maximum occurrence of soluble calcium salts.

With depressed pyrite oxidation, caused by the MgO addition, the outgo of magnesium from the light addition showed a gain of but 2993 pounds for the 5-year period, as against the larger increases of 4608 pounds for the sulfate addition and 4922 pounds for the rapidly oxidized sulfur. The annual losses from the light MgO decreased yearly after the maximum of the first year.

In the case of the heavy lime tank 65, there was a very positive depression in magnesium outgo. As previously shown by lysimeter-leaching data (7), there was a minimum of calcium sulfate in the solution phase to effect basic replacement. If the total pyrite addition had been oxidized 4246 pounds of calcium sulfate would have been present. Its tendency toward magnesium liberation would, however, have been nullified by the excess of CaO, as is shown by the practically identical depression in outgo, 259 pounds, or a decrease of 276 pounds below the 535-pound outgo from the no-treatment control caused by the same calcic treatment when used in connection with the soluble sulfate.

It has been pointed out (7) that the 32-ton MgO addition was decidedly depressive upon the oxidation of pyrite. Consequently, in this instance, less of magnesium sulfate was present to function as a calcium liberant. As would be expected, a large amount of magnesium bicarbonate was leached following the conversion of the excess of oxide to carbonate. It was noted previously in this contribution that the effect of the excessive outgo of magnesium bicarbonate, or that of the excess of residual $\text{MgO-Mg(OH)}_2\text{-MgCO}_3$, was to decrease materially the outgo of calcium salts derived from native calcic materials.

Sulfur-oxide group

In agreement with the FeSO_4 and pyrite controls, the unsupplemented sulfur addition gave a material increase in magnesium outgo. This increase may be charged to the rapid oxidation of the elementary sulfur, as was shown in previously reported (7) sulfate-outgo results.

The light CaO treatment resulted in a distinct acceleration of the oxidation of the added sulfur and in the formation of calcium sulfate. This increase is reflected in the failure of the light lime addition to show a depressing effect upon magnesium outgo. The smaller increase of 53 pounds, as compared with the 159-pound and 228-pound increases from the FeSO_4 and pyrite parallels, may be accounted for by the fact that the light addition of lime with sulfur gave a rapidity of sulfate outgo which was intermediate between the other two. The sulfate radical from the sulfur with light lime was most probably generated at a speed which caused it to react primarily with the calcium oxide, and in small measure with native magnesian complexes. The entire amount of oxidized sulfur may, however, have combined with the added calcium, in which case the resultant calcium sulfate—4246 pounds—would have effected basic interchange in the absence of added lime in sufficient excess to be depressive to magnesium outgo.

The light MgO proved even more accelerative to sulfification, and, as is known from unpublished data, to nitrification also. The 4922-pound excess of magnesium outgo over the control, represents the 3750-pound addition plus 1172 pounds of magnesium native to the soil. The enhanced outgo of 4922 pounds of CaCO_3 equivalence calculates to 5906 pounds of MgSO_4 which would account for 1574 pounds of sulfur. The total 5-year outgo of sulfate sulfur from this tank was, however, only 1136 pounds (7), of which 257 pounds was accounted for by rainfall. The 1172-pound excess above the control outgo and 3750-pound addition was attributable therefore not only to enhanced sulfification, nitrification, and CO_2 generation, as the products of these activities may have been neutralized by the MgO addition, but also through the combined influence of the same activities upon non-carbonate magnesian material native to the acid soil. In other words, the light magnesia addition not only suffered complete removal, but it so stimulated soil activities as to cause a further outgo of native magnesium.

In agreement with the corresponding heavy lime additions of tanks 60 and 65, and with previously reported data (10) upon the same treatment at the same rate without sulfur, the 32-ton addition of tank 70 has proved depressive to the leaching of magnesium for each year, the total depression for the 5-year period amounting to 281 pounds. Agreeing also with previous findings (6, 7), carbonation of $\text{Ca}(\text{OH})_2$ was precedent to accelerated outgo of sulfates.

The 5-year total outgo from the 32-ton MgO treatment was practically the same as that from the same treatment when it was used in conjunction with pyrite. In the case of the sulfur supplement, both speed and aggregate of

sulfate outgo were much greater than in the case of the MgO-pyrite combination. A larger proportion of magnesium sulfate and a smaller proportion of bicarbonate is therefore accredited to the sulfur plus heavy MgO, since the determined difference in nitrate leachings was insufficient to be considered as a factor in this connection. On the other hand, practically all of the applied soluble sulfate was removed by the heavy MgO addition during the first year. The smaller total of 18,379 pounds may be accounted for by the probability that the sulfate addition was depressive, initially, at least, to the generation of CO_2 , which depression caused a lesser outgo of magnesium bicarbonate.

CALCIUM-MAGNESIUM TOTALS LEACHED FROM THE LIMESTONE-DOLOMITE-OXIDE GROUP

The most common application of ground limestone is two tons per acre every four or five years, while burnt lime is generally applied at the 1-ton rate. Very few data are available as indicative of the calcium-magnesium losses from the *surface zone*, where many plants feed most extensively. The foregoing discussion shows that the problem of liming is a dual one of calcium-magnesium conservation. Total calcium-magnesium results from the most generally used economic applications and the 3750-pound addition, as approximating the 2-ton CaO addition, which is often made, are of particular interest. It will be remembered that for a given rate, all treatments in this experiment were of constant chemical equivalence.

At the 1-ton oxide-equivalence rate, all treatments gave combined alkali-earth losses in excess of those from the control; but the proportions of calcium to magnesium in the totals varied widely. It should be stressed that from much parallel work with the same type of soil and the same additions, it is known that all of the added calcic and magnesian treatments were quickly fixed as non-carbonate forms by this soil. The leachings were therefore derived from the reversal of the absorption processes, as a result of the action of carbonated water of the soil upon the calcium-silica complexes, except where biologically engendered acids may have acted directly upon the alkali-earth silicates. With this thought in mind, we observe that the 410-pound increase from burnt lime is due entirely to enhanced calcium outgo, since the magnesium leachings were less than those of the control. In a similar manner, it appears that the 451-pound increase accredited to the limestone is also due solely to calcium, since the magnesium leachings were within 8 pounds of those from the control. On the other hand, there came from the MgO addition a 603-pound excess over the total outgo from the control, which excess is attributable entirely to augmented outgo of magnesium, for the 750-pound calcium outgo is 481 pounds less than that from the control. Likewise, we find that the dolomite gave an increase which is attributable solely to magnesium. However, the dolomite addition proved less repressive than MgO upon calcium outgo. This may be due to the formation of a dual salt when the calcium and magnesium of the dolomite are absorbed by the soil. The dolomite contains the two

elements in nearly equivalent amounts, as contrasted to the mass of magnesium and near-absence of calcium in the case of the MgO addition.

When applied at the 3750-pound rate, both oxides gave total calcium-magnesium yields in excess of the near-constants from the four materials at the 2000-pound rate. The MgO showed a more rapid and greater total leaching, as it did also at the 2000-pound rate and as it has done for all rates with this and a similar soil (10). The full increase of 1261 pounds from the 3750 pounds of CaO is due entirely to increased CaO from the addition, for the magnesium outgo was depressed below that of the control. Conversely, the outgo of magnesium from the corresponding magnesia addition accounted in full for the increase of 1796 pounds in total outgo because the calcium leachings were depressed 509 pounds by the 3750 pounds of MgO.

From these data it is evident that equivalent and well-disseminated amounts of CaO, limestone, and dolomite at the 2000-pound-equivalent rate were responsible for practically identical amounts of total calcium-magnesium salts. The ratio of the leached bases varied, however, with consequent change in ratio of residuals and possibly also their availability. The imposed conditions differ from those of the excessive carbonate additions, considered in a previous contribution (10), where the unabsorbed excesses were such that the gaseous phase carbon dioxide was the limiting factor. In the present case the treatment was so limited as to insure complete absorption by the soil, and the dispersion throughout the mass was so thorough that the bulk of the addition and its absorption products represent the controlling factor. Assuming equivalent quantities of CO₂ for the 2000-pound and 3750-pound additions of CaO and MgO—though the heavy treatment may have been more potent in generating carbon dioxide—it appears that the larger addition insured so much wider and more uniform distribution that the available carbon dioxide had a better chance to function in the formation and leaching of bicarbonates.

Another point is suggested relative to the conservation of calcium and magnesium. The CaO, limestone, and dolomite additions of chemical equivalence show 5-year calcium-magnesium losses of about one-fifth of the respective incorporated materials. Were this rate of outgo to continue, the additions would require at least twenty-five years for their dissipation. But, since the increases over the control calcium-magnesium total are progressively decreasing, it is probable that a much larger period would be required for the removal of the additions through leaching. In practice, however, we find that a 2000-pound CaO-equivalent addition should be repeated every four, five or six years, depending upon soil type, composition, method of handling, cropping, topography, and rainfall. With the large part, nearly four-fifths, of the added materials still present in this case, it appears that as the time increases, the absorbed materials become more complex, less soluble, and more nearly corresponding to the availability of the long-aged natural non-carbonate alkali-earth occurrences native to the soil. In other words, the residuals of additions are subject to dynamic conditions and to aging, through which process

they become more and more insoluble and unavailable, and hence of lessened ability to maintain conditions of fertility.

Applying the findings to this particular soil, the response of which to liming under field conditions is known, infertility would be eliminated by the liming material during some rather immediate period after its incorporation in the soil. Recurrence of what would be, in effect, lime poverty would follow because the aging of the absorbed residual from the addition. As corollary evidence derived from the same type of soil the aging of an excess of magnesium has caused transition of toxicity into fertility (9). In this latter case an 8-ton CaO-equivalent of $MgCO_3$ was found to be lethal to tall oat grass several months after the carbonate had been completely fixed or silicated in the soil. About one year later, however, the non-carbonate residual proved beneficial, rather than toxic, though most of added magnesium was still present.

An additional practical application follows from the results, in so far as other similar soils may react with economic amounts of calcic and magnesian materials. Where a crop has a need for magnesium, that earthy alkali should be applied. For such a need will not be cared for through basic interchange in the surface soil, following additions of high-calcic materials. Rather, a decrease in magnesium solubility follows. In a similar manner magnesium additions tend to decrease the solubility of native calcic materials in the soil. Both limestone and dolomite exert some depression, but they are relatively inactive in this regard, as compared, respectively, with burnt lime and burnt magnesia. A later report of work now under way for over two years will give further data relative to the activity of burnt dolomite in this respect. It is quite probable that the results here reported will materially aid in the practical usage of calcareous and dolomitic products used with tobacco and similar crops, which may be subject to chlorotic magnesium deficiency, described by Garner and others (1).

SUMMARY

Leaching data from twenty-two lysimeters over a 5-year period are reported. Limestone, dolomite, CaO, and MgO unsupplemented were added in equivalence to 2000 pounds of CaO per 2,000,000 pounds of soil. Both CaO and MgO were also used unsupplemented at the rate of 3750 pounds. At the same rate and also at 32-ton rate, the two oxides were used with a 1000-pound constant of sulfur added as $FeSO_4$, pyrite and elementary sulfur. Many points as to periodicity of leachings are included in the text, but totals only will be stressed in the summary.

The completely absorbed limestone addition increased the calcium outgo and had no positive effect upon magnesium leachings, while the dolomite addition decreased the calcium outgo and increased magnesium leaching.

Both CaO additions increased outgo of calcium and depressed that of magnesium.

Both MgO additions depressed decidedly the outgo of calcium, while increasing that of magnesium.

FeSO_4 , unsupplemented, increased the loss of native calcium and magnesium. When supplemented with the light CaO addition, it doubled the increase in outgo of calcium. The CaO supplement depressed the solvent action of the FeSO_4 upon native magnesium. Although increasing magnesium outgo, the light MgO addition was repressive to the solubility of native calcium. The heavy CaO supplement to FeSO_4 increased the calcium outgo and depressed that of magnesium to a point below the outgo from the control. Conversely, the heavy MgO supplement nullified the replacement tendency of MgSO_4 and depressed the outgo of calcium by 822 pounds.

The unsupplemented pyrite acted as did FeSO_4 upon native calcium and magnesium. The light CaO also acted as it did when used as a supplement to FeSO_4 , by accelerating calcium outgo and repressing the liberative tendency of the engendered CaSO_4 . Conversely, light MgO , with pyrite, served to depress calcium outgo below that of the control, while increasing magnesium leachings. The heavy addition of CaO gave enhanced yields of calcium, but positive depressions of native magnesium outgo. In similar manner the heavy MgO supplement, with pyrite, was responsible for a marked decrease in calcium outgo, along with enhanced losses of magnesium.

Sulfur alone caused increased losses of both calcium and magnesium, the losses agreeing closely with those from the FeSO_4 and pyrite controls. The leachings from the light addition of lime with sulfur contained still more of calcium and less of magnesium. The light addition of MgO increased magnesium losses and almost nullified the liberative activity of the MgSO_4 formed by the accelerative action of magnesia upon the oxidation of the sulfur addition. The heavy lime treatment acted as it did with the other two sulfur carriers by increasing calcium losses and depressing magnesium outgo. Again, the heavy MgO supplement, with sulfur, exhibited a distinctly retardative effect upon calcium outgo, while increasing the leaching of magnesium.

The 2000-pound-equivalent additions of CaO , limestone, and dolomite gave near-equal calcium-magnesium totals. The increases from these treatments amounted to only about one-fifth of the amounts added. The increases from CaO and limestone were due entirely to calcium, while those from dolomite and MgO , were due to enhanced losses of magnesium, the calcium outgo having been less than that of the control. The 3750-pound additions of CaO and MgO proved augmentive to totals, but reciprocally depressive upon outgo of native materials.

The losses of about one-fifth of the total unsupplemented additions at the 2000-pound rate, and the progressively decreasing leachings, indicate that after absorption the added calcium and magnesium undergo aging and consequent decrease in solubility and availability. Such a result would be anticipated only where silicate complexes occur in considerable proportions.

Possible practical applications of the findings are mentioned.

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COMPARISON OF THE SOIL SOLUTION BY DISPLACEMENT METHOD AND THE WATER EXTRACT OF ALKALI SOILS

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For the purpose of this discussion, the expression "soil solution" means the watery solution obtained from moist soil by the displacement method as described by Burd and Martin (1, 2). The water extract of the same soils was made at the same time from another portion of the same homogeneous mass of soil by mixing with five times its weight of distilled water nearly free from CO_2 and filtering through Pasteur filters. The procedure was essentially that of the United States Bureau of Soils (4, p. 10).

DESCRIPTION OF THE SOILS USED

Soils 18, 19, 20 and K are fine sandy loams from Kearney Vineyard near Fresno. They are very similar physically. Chemically, they differ in amounts of alkalinity and salinity. Soil 18 is highly saline, not alkaline. The others are somewhat alkaline and highly saline, except K, which is the same soil as 19 after most of the easily soluble matter had been removed by flooding and leaching in the field. Soil Imperial is a fine sediment containing considerable CaCO_3 . It is a composite of samples from Imperial Valley. Soil R is somewhat similar to Imperial physically and contains some CaCO_3 , but is probably residual. It is found near Riverside. Soil Colusa is a composite of samples of Willows adobe clay, obtained near Cortena. Soil S1 is a sedimentary clay loam from Sutter Basin. Soil S2 is similar to S1, from the same locality, but contains less salts and more alkalinity. It is very much deflocculated, hence the solutions from it are obtained with great difficulty.

METHOD OF OBTAINING THE DISPLACED SOLUTION

The soil, previously moistened to about optimum for plant growth, is packed tightly into a brass tube three inches in diameter, seventeen inches long. The lower end is closed by a screw cap which supports a wire gauze and filter paper on which the soil rests. After the soil is packed into the tube, about 500 cc. of water are placed on top of the soil and the tube is screwed into the pressure apparatus. When it has stood thus a few hours to permit the water to diffuse into the upper soil, air pressure is applied to force the solution out at the lower end of the tube. The percolate is collected in aliquots of 5-25 cc. The electrical conductivity of each portion is determined. This is nearly constant so long as the solution is not mixed with the displacing water. A considerable change in conductivity is evidence that the true soil solution is no longer being obtained. All the like portions of solutions are united to make the solution that is to be analyzed.

The analytical methods employed were those commonly used and known to give accurate results. All quantities were found by actual determination, none

by difference. Few determinations were duplicated, but the accuracy was checked by the "reaction values".

In most cases, the error of analysis was well below 5 per cent. On account of having available only very small volumes of some of the solutions, it was not possible to repeat analytical work, and considerable percentage error is to be expected in determination of such small amounts as are involved in some of these cases.

The method of calculating and using "reaction values" is given by Chase Palmer (3). By this means, the reacting power, or combining capacity, of each ion in the solution is given a numerical representation, expressed as percentage of the reacting power of all the ions in the solution taken as 100 per cent. This permits giving the chief properties and general character of the water numerical representation so that one is readily compared with another by actual figures.

THE RESULTS OF THE ANALYSES

The figures in table 1 express the results in parts per million. In line A are given the amounts found in the 1:5 water extract as parts per million of the oven-dry soil. In line B shows the amounts given in line A as parts per million of the water which the soil contained at the time it was weighed out for analysis. In line C are given the amounts found in the displaced solution. Now if there were no interfering factors, the quantities in lines B and C should be substantially alike. But in many respects, they are unlike, so that it appears that the water extract does not truly represent the soil solution. A brief consideration of the results will bring out the differences and relationships.

Calcium. There seems to be no apparent relation between the amounts of calcium found by the two methods, as exhibited in lines B and C. It might be expected that in a nearly neutral soil they would be similar, while in an alkaline soil more calcium would be found in the water extract than in the displaced solution because of the greater dilution. The figures obtained do not support this view. The amounts of calcium found in soils 18, K, Imperial, R, S1 and S2 are somewhat similar in B and C, yet some are alkaline, some nearly neutral. For soils 19, Colusa and 20, the displaced solutions contained much more calcium than the water extracts.

Magnesium relations are equally inexplicable. No law is apparent.

Sodium. With the exception of soil Colusa, sodium found in the water extract is two to four times as much as in the displaced solution. This is probably due to hydrolysis of easily decomposed silicates in the presence of the larger proportion of water used for the water extract.

Potassium. Except in soils S1 and S2, potassium is much less in the displaced solution than in the water extract. It acts like sodium. The exception in case of S1 and S2 is seemingly unimportant, since the amounts found are almost within the limits of experimental error. The fact that more water

dissolves more potassium is of interest in plant nutrition, as indicating that more of this element may be made available by suitable soil treatment.

Carbonate. This ion is evidently dissolved in proportion to the amount of water used, since the water extract contains much more than the soil solution. The small amounts shown in line C for soils 19, K, Imperial, Colusa and S1, may be due to the solubility of CaCO_3 in the relatively greater concentration of sodium salts in the displaced solution. The water extract is likely to give a very erroneous idea of the concentration of carbonate in the actual soil solution.

Bicarbonate. This ion is misrepresented by the water extract even more than the carbonate ion. The actual soil solution is much better for plants than would appear from examination of the water extract. Bicarbonates are relatively insoluble.

Sulfate. Two or more times as much sulfate is found in the water extracts as in the displaced solution.

Chloride is more nearly similar in the two solutions, though somewhat lower in the displaced solution.

Nitrate is also much alike in both. The apparent exceptions are probably due to imperfections in analytical work, and unrepresentative character of the solutions analyzed.

Phosphate appears to form a saturated solution in all cases, so that the amount found by analysis depends on the amount of water used in making the solution. The amounts found were within the limits of analytical error in some cases, so that it is not certain that there was any phosphate at all in some solutions.

ACTUAL CONCENTRATIONS IN THE DISPLACED SOLUTIONS

To one who is in the habit of considering the amounts found by the water extraction method calculated to the weight of dry soil, the concentration of solutes in the displaced solution may appear very great. Yet this latter is essentially the solution from which plants must draw their mineral nutriment. When one realizes the osmotic pressure and the possibly caustic or corrosive character of the displaced solution from some of these saline or alkaline soils, it is much more apparent why such soils are a very unsuitable medium for support of plant life.

GEOCHEMICAL CLASSIFICATION OF THE SOLUTIONS

A cursory examination of the analytical results shows that there is a larger proportion of the salts of calcium and magnesium in the soil solution than in the water extract. But when the solutions are classified according to the system proposed by Palmer (3) their relations and differences become much more evident (see table 2). According to this system, non-hydrolyzed salts produce salinity, hydrolysable salts cause alkalinity of water solutions. In either case, sodium and potassium give primary salts, calcium and magnesium

TABLE 1
Solutes in alkali soils

	SOIL NUMBER	MOISTURE per cent	Ca	Mg	Na	K	CO ₂	HCO ₃	SO ₄	Cl	NO ₃	PO ₄
			p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
A	18	16.2	351	130	1,426	86	0	222	739	1,193	2,165	10
B			2,160	802	8,798	529	0	1,375	4,550	7,313	13,358	62
C			2,770	972	5,350	248	0	427	2,152	6,600	13,200	3
A	19	12.8	12	10	934	47	0	493	717	705	183	22
B			94	78	7,294	367	0	3,850	5,580	5,520	1,430	172
C			740	238	4,614	178	24	1,520	4,403	4,850	1,116	4
A	20	12.8	24	4	1,695	81	106	336	680	1,600	683	34
B			188	31	13,250	683	827	2,650	5,310	12,500	5,340	265
C			510	146	10,050	530	85	830	3,839	11,370	4,452	9
A	K	11.7	104	12	216	23	0	225	602	35	21	8
B			889	102	1,845	196	0	1,920	5,152	298	179	68
C			700	79	998	68	Tr.	622	3,222	30	87	0
A	Imperial	20.5	65	21	582	39	0	314	844	236	209	4
B			317	103	2,840	190	0	1,522	4,118	1,150	1,020	19
C			540	160	940	64	Tr.	158	2,304	850	223	?
A	R	16.1	37	81	4,220	470	246	255	4,278	3,260	835	3
B			229	502	26,400	2,940	1,525	1,585	26,500	20,300	5,170	19
C			225	702	20,525	2,110	183	561	21,644	17,500	4,191	5
A	Colusa	25.5	261	130	115	85	0	507	4,660	522	35	4
B			1,023	509	450	333	0	1,980	18,267	2,050	137	16
C			470	365	2,750	21	49	244	6,090	1,570	?	?

A	S1	23.8	259	172	669	25	0	126	651	1,365	104	2
B			1,085	722	2,820	105	0	530	2,740	5,720	437	8
C			1,410	852	1,230	170	Tr.	244	2,035	5,265	?	2
A	S2	19.7	13	12	533	22	78	905	174	129	40	19
B			66	61	2,970	111	395	4,580	682	655	203	96
C			90	48	1,010	210	210	1,249	857	342	?	?

A = amount found in 1:5 water extract, calculated to dry soil

B = same, calculated to water in soil at time of extraction

C = amount found in the displaced solution at same time

secondary salts. When the sum of the reaction values of all the ions in a solution is regarded as 100 and the percentage of the whole in primary and secondary salinity, and primary and secondary alkalinity is calculated, the relation between the composition of the water extracts and the displaced solutions is clear. With little exception, the water extracts have higher primary and lower secondary salinity than the displaced solutions. Concurrently, the water extracts have higher secondary alkalinity than the displaced solutions.

TABLE 2
Geochemical interpretation of the analyses

SOIL NUMBER	METHOD OF OBTAINING THE SOLUTION	SALINITY		ALKALINITY	
		Primary	Secondary	Primary	Secondary
18	Extracted	71.4	21.8	0.0	6.8
	Displaced	52.8	44.8	0.0	2.4
19	Extracted	83.6	0.0	14.4	3.0
	Displaced	70.4	17.6	10.0	2.0
20	Extracted	88.8	0.0	9.2	1.9
	Displaced	92.0	4.4	0.0	3.3
K	Extracted	62.8	18.8	5.6	17.4
	Displaced	49.4	38.4	0.0	11.8
Imperial	Extracted	80.6	4.2	0.0	16.2
	Displaced	52.8	43.2	0.0	3.2
R	Extracted	94.4	0.0	0.8	4.1
	Displaced	92.0	6.5	0.0	1.5
Colusa	Extracted	78.8	15.2	0.0	7.0
	Displaced	69.0	28.6	0.8	2.2
S1	Extracted	52.6	43.1	0.0	3.7
	Displaced	29.4	67.9	0.0	3.4
S2	Extracted	32.3	0.0	61.3	6.4
	Displaced	50.3	0.0	33.7	15.0

Secondary salinity is preferable to primary, in arable soils, therefore the picture presented by the water extract is less favorable than that given by the displaced solution. The actual condition in the soil is better than is indicated by the water extract. Secondary alkalinity is desirable, primary alkalinity very injurious to soil. In this respect, the displaced solution indicates that the actual condition in an alkali soil is worse than would be expected from an examination of the water extract. Thus the water extract considerably misrepresents the actual conditions in an alkali soil. But it will be observed that

the total alkalinity, sum of primary and secondary, is without exception, much less in the displaced solution. So, on the whole, the displaced solution gives a considerably better notion of actual conditions in the soil, and a much more favorable impression as to the suitability of the soil for the support of plant life. It seems probable that the larger proportion of calcium and magnesium in the true soil solution is due simply to the greater solubility of their salts in solutions of sodium salts, than in water alone.

Either method may be expected to reveal the principal defects of an alkali soil such as an excess of water soluble salts, or a low hydrogen-ion concentration whereby Ca, Mg, Fe and PO_4 are likely to be rendered unavailable to plants. One thing in which the displaced solution is decidedly superior is in the comparatively true representation of the actual concentration of solutes in the soil solution. The water extract will not give a correct impression unless the amounts found are calculated back to the concentration they would have in the actual soil moisture, and in the case of most of the ions, except Cl, NO_3 and perhaps Na and K, this is likely to give a distorted picture of actual conditions.

SUMMARY

1. Nine different alkali soils have been examined by the two different methods, water extraction and displacement, and the analytical results on the two solutions compared.

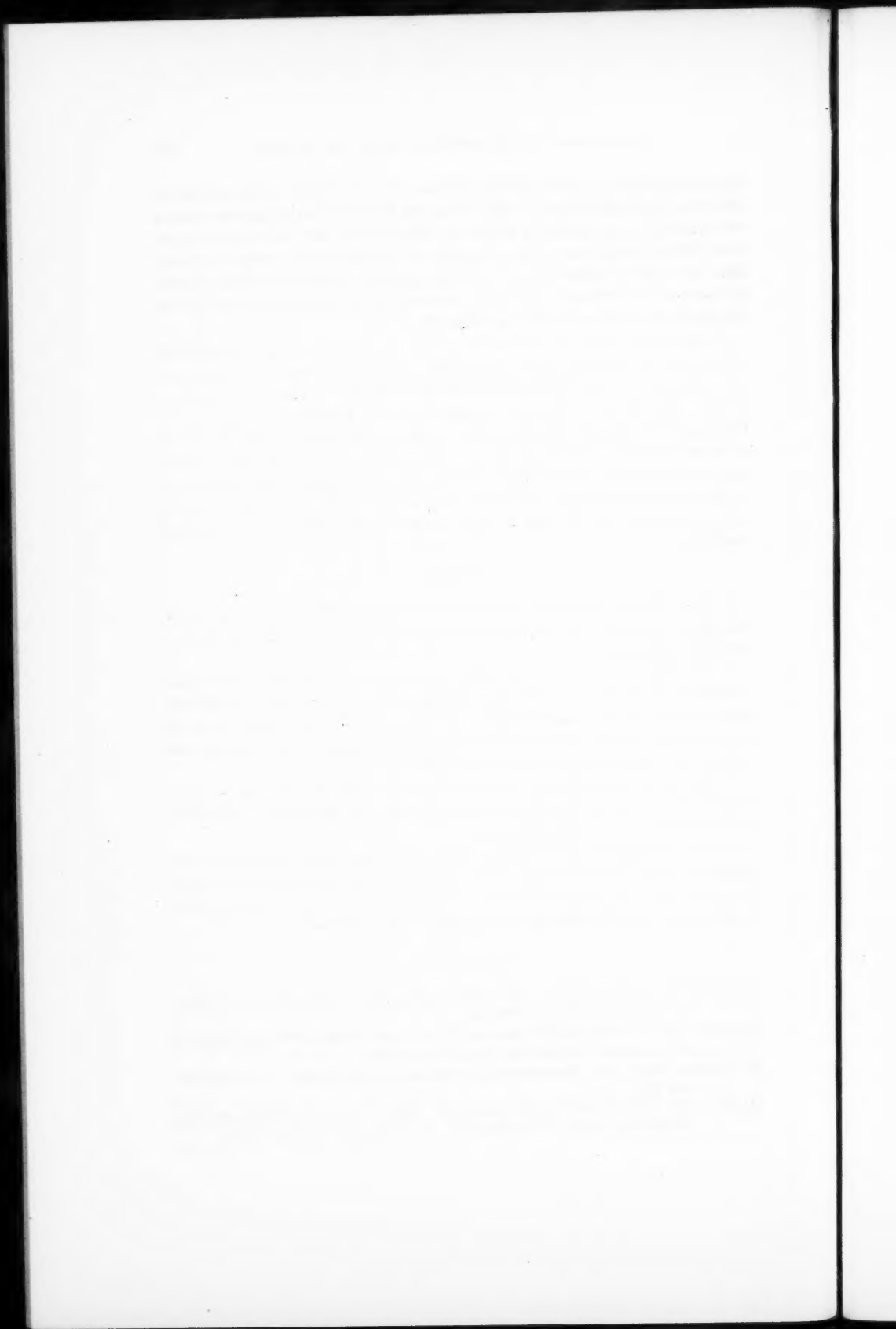
2. The data indicate that the water extract does not represent the actual conditions in the soil. Carbonate, bicarbonate, and phosphate are greatly overestimated in the water extract. Chlorine, nitrate and sodium may be approximately correct, sulfate and potassium are much overestimated, and calcium and magnesium may be either high or low.

3. The actual concentration of solutes in the true soil solution may be much greater than is generally realized by one accustomed to thinking in terms of the amounts found in 1:5 water extracts.

4. The geochemical classification shows that the water extracts contain relatively larger proportions of sodium salts and less of calcium and magnesium salts than the true soil solution. The latter makes the soil appear more favorable for plant life than does the water extract method.

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THE HYDROCHLORIC ACID METHOD FOR DETERMINING IN THE SOIL THE CATIONS PRESENT IN AN ABSORBED CONDITION

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A detailed method has been worked out for determining in the soil those cations which are present in the organic and mineral parts of the soil in an absorbed condition; by replacing them with the ammonium ion of ammonium chloride (1). This method is basic, since it doubtless gives the kind of cations present in the soil in an absorbed condition and their concentrations. But this method has its faults: It requires a considerable period of time, is expensive and the determination itself of the bases extracted from the soil by a solution of NH_4Cl represents certain difficulties due to the presence of large quantities of NH_4 in the solution.

The author's investigations (soon to be published) on the action of cold, dilute concentrations of hydrochloric acid upon the soil, suggest a simpler, more convenient and cheaper method. The method is based upon the fact that, on treating the soil with HCl not stronger than 0.05 N, there is an exchange of cations between the hydrochloric acid and the zeolitic-humic part of the soil, but not the formation of a solution.

The analysis is carried out as follows: 5-25 gm. of soil, depending on the abundance of absorbed bases in the soil and details of analysis, are treated in the cold with 25-50 cc. of 0.05 N HCl (exactness is not necessary here) in a small porcelain dish, and the suspension is then transferred upon a filter, (hardened paper no. 602) in a funnel, using the same acid; the soil is then washed with the same acid until the filtrate shows no trace of calcium. It is useless to make the test before about 300 cc. of filtrate is obtained. In making the test, one has to keep in mind that the HCl extracts some aluminum; it should, therefore, be carried out as follows: the filtrate is neutralized with ammonia, warmed to boiling, some oxalic acid is added until all the precipitated $\text{Al}(\text{OH})_3$ is redissolved, then some ammonium oxalate is added.

The filtrate is treated as follows: it is evaporated to dryness on addition of some nitric acid, the organic matter is destroyed with aqua regia; the residue is dried for 30 minutes at 125-150°C., is dissolved in dilute HCl on warming and the SiO_2 is filtered off. To determine calcium and magnesium in the filtrate, the iron and aluminum have to be precipitated out; about 10 cc. of

1.0 N solution of NH_4Cl should be added to the liquid to make the filtration of the higher oxides. In determining the alkalies, the higher oxides and magnesium are separated by lime water. All these operations are carried out as soon as possible, since it is easy to contaminate the replaced bases by others.

There is basis to suppose that in soils greatly podsolized, where it seems that the formation of new absorbing complexes takes place in several horizons, the hydrochloric acid, even in the low concentration, may destroy to a certain extent this newly formed mineral-organic complex.

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SOIL FLORA STUDIES

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There are three distinct groups of organisms common to an ordinary soil which can readily be distinguished on gelatin plates. The names that have been applied to these groups are: actinomyces, non-spore-formers, and spore-formers. Much interesting information has already been gained concerning these organisms but there are still many things which need investigating. The author thought that some interesting data could be procured from a study of the effect, on the groups, of green manure at different stages of growth. The following experiment, therefore, was performed.

Rye, oats, and buckwheat were harvested at three different stages of growth, and cut into pieces about one inch in length. These pieces were incorporated with soil at the rate of five tons of green manure to the acre. The soil was then put into gallon pots filled with Dunkirk clay loam. Two series differing in decomposition periods were run. One was allowed to decompose for twelve months, the other for four months. The moisture content was kept at twenty-five per cent (dry basis) and a temperature of 28°C. was maintained in the green house during the whole experiment. After this incubation treatment, samples were taken and dilutions made at the rate of 1-100,000. All treatments were made in triplicate and for each pot triplicate gelatin plates were poured, thus giving nine poured plates of each manuring treatment. The medium was made with 1000 cc. tap water and 120 gm. of gelatin. The reaction of this medium was 0.005 *N* acid to phenolphthalein. The plates were incubated at 18°C. for 10 days. Counts were then made of the three groups of organisms, i.e., actinomyces, non-spore-formers, and spore-formers.

From the data presented it will be noted that:

1. The non-spore-formers are in a majority in a normal soil.
2. When green manures were added there were usually more total organisms.
3. In general the younger the manure added, the greater the numbers of actinomyces developed in proportion to other organisms.
4. Spore-formers were influenced proportionately less than the others.
5. The actinomyces group was influenced to the greatest extent.

These results seem to indicate that perhaps the particular function of the actinomyces group of organisms is that of cellulose decomposition.

Inasmuch as the three groups are constant for a normal soil,—and it appears that each outside influence has a specific effect upon the ratios of the groups,—perhaps a study of the effect of the numerous types of soil treatment may show as many different ratios. If so, this would aid in interpreting various soil phenomena or, at least, suggest a mode of attack in the solution of some of our soil problems.

TABLE 1

Organisms per gram of dry soil after treatment with rye as a green manure

STAGE OF GROWTH OF RYE	AVERAGE NUMBER OF ORGANISMS PER PLATE		
	Actinomyces	Nonspore-formers	Spore-formers
<i>After twelve months humification</i>			
Check.....	1,900,000	2,000,000	300,000
Boot stage.....	2,371,200	2,918,400	729,600
Well headed.....	1,750,000	675,000	500,000
Almost ripe.....	1,200,000	650,000	300,000
<i>After four months humification</i>			
Fully headed.....	5,000,000	4,300,000	400,000
Heads turning yellow.....	3,200,000	1,900,000	500,000
Ripe.....	2,000,000	2,000,000	200,000

TABLE 2

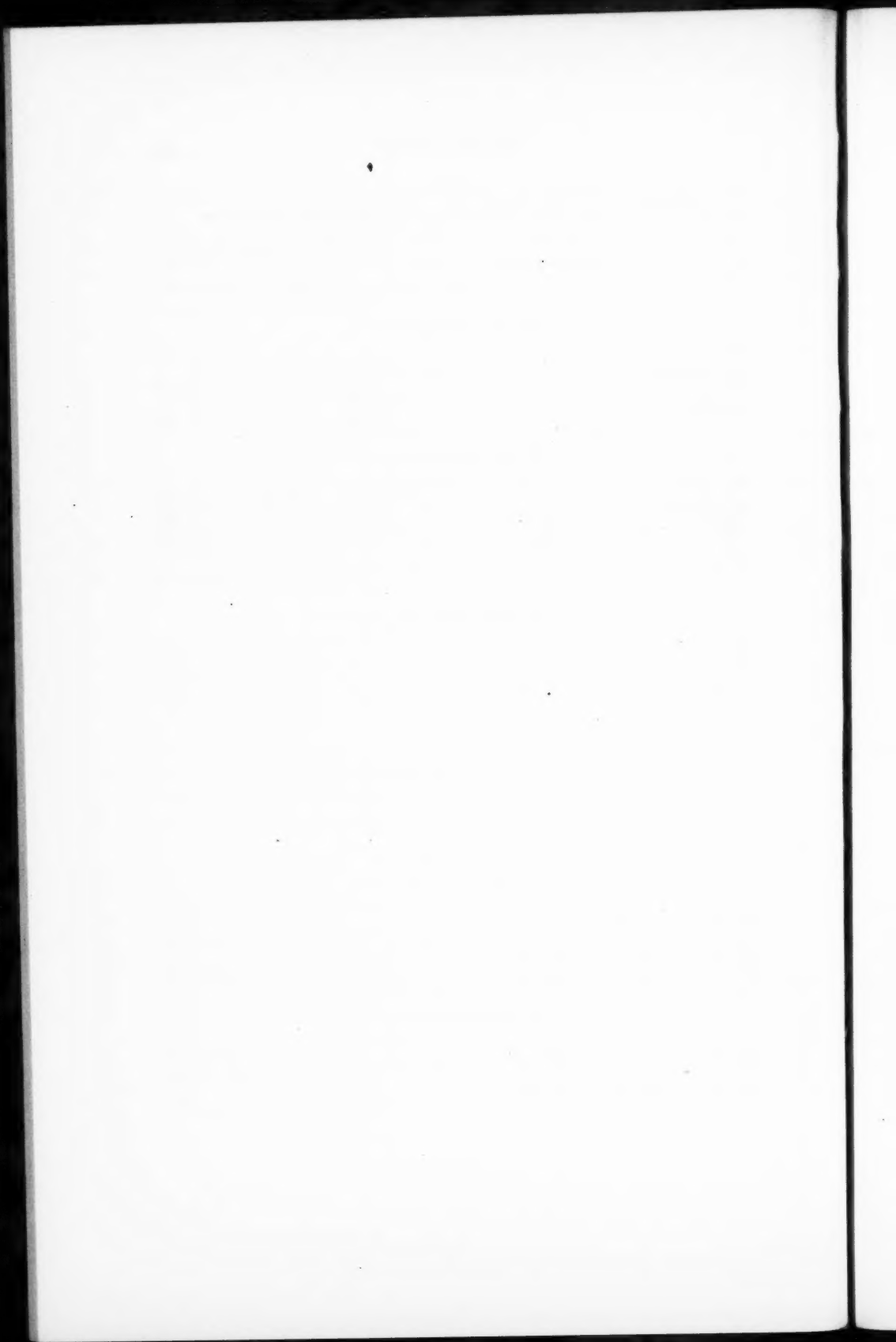
Organisms per gram of dry soil after treatment with oats as a green manure

STAGE OF GROWTH OF OATS	AVERAGE NUMBER OF ORGANISMS PER PLATE		
	Actinomyces	Nonspore-formers	Spore-formers
<i>After twelve months humification</i>			
Check.....	1,900,000	2,000,000	300,000
Preceding boot stage.....	2,100,000	650,000	300,000
Late boot stage.....	1,800,000	450,000	260,000
Almost ripe.....	1,500,000	400,000	210,000
<i>After four months humification</i>			
Well headed.....	3,000,000	2,300,000	200,000
Turning yellow.....	2,700,000	1,700,000	300,000
Ripe.....	1,900,000	1,500,000	300,000

TABLE 3

Organisms per gram of dry soil after treatment with buckwheat as a green manure

STAGE OF GROWTH OF BUCKWHEAT	AVERAGE NUMBER OF ORGANISMS PER PLATE		
	Actinomyces	Nonspore-formers	Spore-formers
<i>After twelve months humification</i>			
Check.....	1,900,000	2,000,000	300,000
Just blossoming.....	3,800,000	900,000	450,000
Well blossomed.....	4,100,000	1,800,000	200,000
Just going to seed.....	3,500,000	1,650,000	175,000
<i>After four months humification</i>			
Well blossomed.....	4,000,000	2,100,000	100,000
Seeds forming.....	6,100,000	2,100,000	200,000
Ripe.....	3,100,000	2,000,000	200,000



STUDIES ON SULFUR OXIDATION IN OREGON SOILS

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INTRODUCTION

Sulfur applied as a fertilizer to certain soils in Oregon and elsewhere has greatly increased crop yields. Several types of soil in both southern and eastern Oregon show remarkable response to elemental as well as combined forms. Increases of 110 to 500 per cent in alfalfa yields are frequently obtained in these sections by comparatively light applications of either flour sulfur or gypsum. That several soil types in these same localities do not respond to sulfur fertilization is hardly less striking, especially in those instances where they are not only apparently similar to adjacent untreated responsive soils, but also practically the same in crop producing power.

The rôle of sulfur in soil fertility is a varied one. Primarily it is an essential plant food element but as such it is available to crops only in sulfate form. Sulfonation, or the oxidation of unavailable forms of sulfur to the available sulfate, results in the formation of sulfuric acid, which affects other constituents and processes of the soil. The accompanying increase in hydrogen-ion concentration also influences the soil as a culture medium, and, as demonstrated by a number of investigators advantage may be taken of this feature to control the potato scab fungus. Sulfur may thus have an indirect, as well as a direct fertilizing action on plant growth. In the instances cited herein its effect is not indirect, judging from evidence at hand.

HISTORICAL

Various sulfur fertilizers, as shown by Brown and Johnson (3) apparently stimulate ammonification in certain soils under laboratory conditions. This has been confirmed by Ames and Richmond (2) and by Ames (1) but these investigators found that in both acid and alkaline soils as ammonification was increased nitrate formation was decreased, the depression being less as acidity decreased and as basicity increased. They have also pointed out that increasing quantities of ammoniacal nitrogen which accompany decreasing amounts of nitrates when sulfur is oxidized cannot be considered as an indication of sulfonation with a stimulating effect on ammonification. The inverse relation between ammonia and nitrates is held to be due to a lack of sufficient basic material to neutralize the sulfuric acid produced in sulfonation, with the result that the ammonia unites with the acid and remains as ammonium sulfate instead of being nitrified. Since alfalfa and clover feed heavily on nitrate nitrogen, therefore thriving to best advantage on slightly alkaline soils, it is apparent that the action of sulfur on ammonification and nitrification is detrimental rather than favorable where these legumes are concerned.

Solvent action of the sulfuric acid produced in sulfur oxidation may increase soil fertility. That sulfonation has a solvent action on unavailable phosphates has been shown by Lipman, McLean, and Lint (7). Nitrogen fixation, symbiotic and nonsymbiotic, may thus be indirectly stimulated; several investigators, notably Ashby, have pointed out that available phosphorus increases this soil function. According to Chauzit (4) the benefits obtained from sulfur fertilization on certain soils in France are due to its rendering soluble and readily assimilable the fertilizing elements of organic matter and some mineral substances. This action, however, varies with the quantity of sulfur applied and with the length of time of contact with the soil, best results having been obtained with 300 to 500 pounds of sulfur per acre applied as far as possible in advance of the time when the plants are most in need of nutritive elements.

REASONS FOR THIS INVESTIGATION

Where applications of only 100 pounds of sulfur per acre to Oregon soils give marked increases in yields over a period of three years, the solvent effect can be of little importance. This is further supported by the fact that response is noticeable within a few weeks after the sulfur is applied in the spring just previous to seeding. Either flour sulfur or gypsum is used in this manner with equal effectiveness. The use of gypsum which is not subject to sulfonation eliminates any solvent action.

It would seem, therefore, that sulfur fertilizers act directly by supplying a limiting plant food element. This is to be suspected also from chemical analyses, which show that the responsive soils are comparatively low in total sulfur, the amounts ranging from 0.006 to 0.024 per cent. The location of these soils precludes any appreciable factors affecting their sulfur content. Not only is the rain-fall light, averaging 17 inches per year in the Medford area, 13 inches in Klamath Falls vicinity, and 8 inches in the Columbia basin region, but it is also relatively low in sulfur content since the regions are sparsely settled and practically free from coal smoke. For the same reason the irrigation water, which comes from melting snow on surrounding mountains, is likewise probably low in sulfur.

Reasons for no response from sulfur fertilizers when applied to certain soils may be several. The soil may contain an ample supply of sulfates, in which case if a low crop-producing power exists there must be some other limiting factor. If a soil responds to sulfate fertilizers but not to elemental sulfur, it is evident that conditions for sulfonation are unfavorable.

Since sulfonation is largely a microbiological process, primarily a function of certain soil bacteria and fungi, any differences in its extent may be due to variations in physiological efficiency or to relative numbers of the microorganisms involved. On this basis inoculated sulfur or sulfur composts containing bacteria of high sulfur-oxidizing efficiency would be of great economic value. In general farm practice an application of this material would be desirable on soils low in available sulfur and low in sulfur-oxidizing efficiency. Its need under Oregon field conditions would be indicated only on soils which respond to sulfates but not to unavailable forms of sulfur.

Variations in physiological efficiency, or in relative numbers of sulfofying organisms, can be ascribed to environmental factors, of which the total sulfur supply in the soil may be important. It is reasonable to suppose that a deficiency of sulfur would at least reduce the number of obligate sulfofiers, probably reduce the numbers of facultative sulfofiers, and also reduce their efficiency as the stimulus for maximum activity would be lacking. An ample sulfur supply, on the other hand, would furnish food for a maximum number of sulfofying microorganisms and enable them to develop their highest efficiency, other conditions being favorable.

The depth and physical condition of the soil must be taken into account, however, when considering the relation of sulfur supply to crop yields. Two soils may show on analysis the same percentage of sulfur but while one may respond to the application of sulfur the other may not solely because of a difference in depth or physical condition. This has been emphasized by Reimer (9), who pointed out that a deep mellow soil provides new feeding areas for plant roots several years after a shallower soil has become exhausted, and that sulfofication is probably able to proceed more rapidly in mellow soils because of better aeration.

PLAN OF INVESTIGATION

To determine any relation that certain factors connected with sulfur supply and sulfur transformation in a soil may have to response obtained from sulfur fertilization, the investigation herein reported was conducted. The specific aims in view were the following:

1. To determine the sulfofying power of representative soil types and to find if this power is low or lacking in types not responding to sulfur fertilization.
2. To find a relation between total sulfur content and sulfofying power.
3. To find a relation between sulfofying power and sulfate content.
4. To find a relation between total sulfur content and sulfate content.
5. To find if any relation exists between the hydrogen-ion concentration and the sulfofying power of the soil.
6. To find any relation existing between the sulfur oxidizing power and the buffer value of the soil.
7. To correlate if possible any relation between the texture of the soil and its buffer value.

COLLECTION OF SAMPLES

Samples of fourteen soil types representative of four distinct areas of Oregon were obtained for study. Except for two samples obtained locally, these were collected and sent in by persons other than the investigator. Clean cement bags were supplied as shipping containers and proper instructions for collection were given to insure representative samples free from undue contamination.

Samples from the irrigated Columbia basin district were sent in by H. K. Dean, superintendent, Umatilla branch experiment station. Southern Oregon samples were furnished by F. C. Reimer, superintendent, Southern

Oregon branch experiment station. F. H. Thomas, county agent for Klamath County, submitted the central Oregon samples. A muck sample, representative of a large area in Marion County, was obtained through C. V. Ruzek, professor of soil fertility, Oregon Agricultural College, and two other Willamette Valley samples were collected on the college farms. A description of the various samples follows.

COLUMBIA BASIN SOILS

1. *Umatilla station, check plot.* Medium sandy soil, which, being light and arid, is naturally deficient in organic matter and plant food. Rotations and feeding of crops on the land are necessary to maintain and increase fertility. Sample taken from a field which has produced alfalfa for ten years.

2. *Umatilla station, sulfured plot.* Same as sample 1 except that sulfur at the rate of 100 pounds per acre was applied in March, 1919, resulting in no increase in yield of alfalfa.

3. *Stanfield project, check plot.* Fine sandy soil of same origin as sample 1 to which it is apparently similar in all characters other than texture. It also has produced alfalfa for ten years.

4. *Stanfield project, sulfured plot.* Same as sample 3 but sulfured at the rate of 100 pounds per acre in March, 1919. A large increase in yield of alfalfa resulted.

SOUTHERN OREGON SOILS

5. *Salem clay loam, check plot.* A deep, fertile, clay loam containing 21 per cent of clay and 40 per cent of silt. Though distinct from adobe it becomes sticky when wet and hard when dry. The potassium, calcium, and magnesium content is high. The nitrogen supply is fair in the surface soil but low in the subsoil. The amount of phosphorus and sulfur present is low. Alfalfa grown on this soil has a pale, yellowish-green color, and the growth is so poor that weeds often outgrow the alfalfa.

6. *Salem clay loam, sulfured plot.* Same as sample 5 but has received two applications of sulfur at the rate of 100 pounds per acre, the first in 1915 and the second in March, 1917. The response to sulfur was remarkable. The alfalfa became a dark, rich green color, grew luxuriantly, and was practically free from weeds.

7. *Medford loam, check plot.* This soil is a deep, fertile, brown silt loam well supplied with potassium, calcium, magnesium and nitrogen. The phosphorus content is low. There is also a deficiency of sulfur. No response has been obtained from any sulfur fertilizer on this soil type.

8. *Antelope clay adobe, check plot.* This is a deep and well drained heavy, black, adobe soil. It has a high water-holding capacity and is of a sticky nature. In late summer it becomes dry and hard and checks badly. Potassium, calcium, magnesium, organic matter, and limestone are present in abundance. The content of phosphorus and sulfur is low. Alfalfa grown on this soil has a pale yellowish color and grows poorly. This crop responded rapidly to sulfur fertilizers with greatly increased yields and a rich, dark green color in the vegetation.

CENTRAL OREGON (KLAMATH COUNTY) SOILS

9. *Allamont ranch, check.* Fine sandy loam taken from a field where no sulfur has been applied. Sulfur applied to adjacent fields has not produced noticeable results.

10. *Case ranch, check.* Fine sandy loam soil which would probably respond to sulfur, judging from increased yields obtained with sulfur on neighboring fields.

11. *Case ranch, sulfured.* Fine sandy loam located near sample 10. Sulfured two years ago at the rate of 100 pounds per acre. Alfalfa yields were increased by the treatment.

WILLAMETTE VALLEY SOILS

12. *Willamette silt loam, check plot.* Brown silt loam soil, well drained, acid in character. It is well supplied with calcium nitrogen, potassium, and phosphorus, and has a fair content of sulfur. Sulfur has been used as a fertilizer on this soil type. The field from which the sample was taken has produced one crop of vetch and oats and one crop of corn. No fertilizers have been applied.

13. *Dayton silt loam, check plot.* A gray soil on stiff, gray and yellow mottled subsoil with poor drainage. Calcium, nitrogen, and potassium are present in ample amounts, but there is a deficiency of both sulfur and phosphorus. Noticeable results are obtained from top dressings of gypsum on clover, 40 to 80 pounds being the usual rate of application per acre. The plot sampled has grown vetch and oats two years and has been top dressed twice with gypsum at the rate of 80 pounds per acre.

14. *Muck.* This soil is high in organic matter and nitrogen content. Sulfur, and calcium are abundant but phosphorus and potassium are low and often limiting factors. Sulfur is not used as a fertilizer on this type, although it is carried in superphosphate, which is frequently used in amounts as high as 500 pounds per acre as a source of phosphorus. The field from which the sample was taken is devoted exclusively to the production of onions.

METHODS

As soon as the samples were received at the laboratory they were air dried, passed through a 10-mesh sieve, and stored in two- and four-gallon glazed stoneware crocks fitted with cardboard covers.

Optimum moisture content for all incubation studies was taken as 50 per cent saturation.

Sulfification. The sulfofying power of each soil was tested by adding sodium sulfide or sulfur to duplicate 100-gm. portions of soil and determining the amount converted to sulfate within a definite period of time, 7-14 days. In some tests 100 mgm. of flour sulfur were used while in others one cubic centimeter of a 10 per cent sodium sulfide solution was used. At the close of the incubation period the soils were tested quantitatively for sulfates by the turbidity method of Schreiner and Failyer (10, p. 54).

Clarification of soil extracts. After water digestion all the soils except the heavy clays gave filtrates more or less yellow in color. Since this color interfered with the turbidity determination for sulfates a means for its removal was imperative.

Bone black was first tried and 2 or 3 gm. of the chemically pure powder was added to the filtrate, which, after thorough agitation, was filtered through a Gooch crucible. This was fairly successful but with the more highly colored solutions the treatment had to be repeated several times to remove the color entirely.

The use of aluminum hydroxide was suggested by the method employed by Emerson (5) for clearing soil extracts for nitrate determinations. A suspension of the hydroxide was prepared from alum according to Emerson's directions but the hydroxide could not be washed entirely free from sulfate. Accordingly, 100 gm. chemically pure aluminum chloride was dissolved in a liter of distilled water and concentrated ammonium hydroxide was then added until precipitation was complete. The precipitate was allowed to concentrate, after which it was transferred to a 3-liter flask and washed three times with 2-liter portions of distilled water, the wash water being decanted after the hydroxide had concentrated to about 1 liter. After the third washing 1 liter of distilled water was added and the pH value adjusted to approximately 7.2 with standard hydrochloric acid. Another liter of distilled water was then added, making three liters of the suspension for use.

Of the thoroughly shaken hydroxide suspension thus prepared, amounts varying from 10 to 20 cc. according to the soil were found to insure colorless filtrates in all cases except with muck, when added to the solutions either at the beginning of digestion or just previous to filtering. Filtrates from muck were readily clarified with 30 cc. of suspension, but amounts up to 60 cc. added before filtering would not give an entirely colorless filtrate.

Total sulfur. The total sulfur content of each soil was determined by fusion with sodium peroxide in an illium bomb (Parr sulfur bomb). This method has the advantage of requiring much less time than fusion in an open crucible, but considerable difficulty was encountered in securing a satisfactory routine and the lack of agreement obtained between duplicates leaves something to be desired. It is probable, however, that had more time been devoted to a study of variations in routine it could have been made to yield results entirely satisfactory. Notwithstanding variations of as much as 20 per cent between duplicates the data may be considered comparative and as serving the purpose of this investigation.

Blank determinations were made to obtain a correction factor for the sulfur in the chemicals used in making up a charge.

Hydrogen-ion concentration. The hydrogen-ion concentration was determined by the colorimetric method. The solutions to be tested were secured by agitating 100 gm. of the soil with 200 cc. of distilled water and removing the soil particles by filtering through filter paper or a Chamberland filter.

TABLE 1
Oxidation of sodium sulfide

SOIL NUMBER	SOIL TYPE	MOISTURE REQUIRED FOR SATURATION	SULFUR AS Na ₂ S OXIDIZED	
			In 7 days	In 14 days
		<i>per cent air-dry wt.</i>	<i>per cent</i>	<i>per cent</i>
1	Medium sand.....	28.1	26	19
2	Medium sand.....	29.7	26	21
3	Fine sand.....	25.9	27	23
4	Fine sand.....	29.4	18	21
5	Clay loam.....	38.7	3	11
6	Clay loam.....	40.7	15	20
7	Loam.....	31.1	10	23
8	Clay adobe.....	52.6	4	8
9	Sandy loam.....	41.4	25	17
10	Sandy loam.....	37.6	16	16
11	Sandy loam.....	40.9	20	18
12	Silt loam.....	50.0	2	30
13	Silt loam.....	40.1	4	8
14	Muck.....	225.5	26	

RESULTS

Oxidation of sodium sulfide. That the water-holding capacity is in inverse ratio with the sulfur-oxidizing power on soils of low organic content is a general conclusion that seems apparent from table 1 and figure 1. This does not hold true for the muck soil 14. Since most Oregon soils are of the semi-arid type and naturally low in organic content this conclusion becomes more significant.

All soils tested showed considerable efficiency in oxidizing sodium sulfide. A greater yield of sulfates was secured in the coarser textured soils. More sulfate was found at the end of seven than at the end of fourteen days in the light sandy soils. It is quite probable that these soils contain very little

buffer hence the hydrogen-ion concentration would soon become strong enough to retard oxidation and possibly favor the development of sulfate consuming organisms.

Sulfonation of flour sulfur vs. inoculated sulfur. The normal Oregon field application of sulfur is 100 pounds per acre. This is applied as long as possible before the crop is planted. In some semi-arid sections county agents are

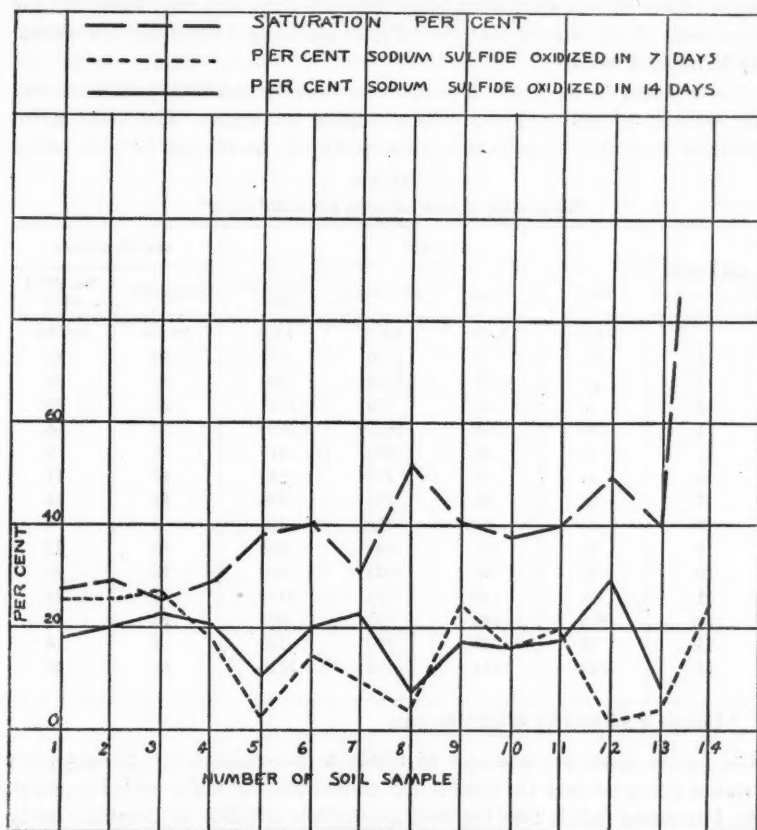


FIG. 1. WATER-HOLDING CAPACITY AND SULFUR OXIDATION

recommending that it be applied in the fall so as to be available for the growing season in the following spring. Under these extensive cropping conditions the fact that a limiting plant food element is being supplied is our great consideration, the control of potato scab and liberation of phosphorus and potassium being of secondary consideration.

Since preliminary tests are showing that even under humid conditions, sulfur is giving some remarkable increases in yield, it becomes of value to determine the rapidity with which the sulfur is oxidized, so as to know how

long before planting the sulfur must be applied. Much waste of soluble sulfates might thus be eliminated. It is under such conditions that a readily oxidizable source of sulfur would prove of greatest value.

The inoculated sulfur tested was supplied through the courtesy of Dr. J. G. Lipman, director of the New Jersey agricultural experiment station. This material seems to be effective in stimulating sulfur oxidation and in several cases it was more completely oxidized than was flour sulfur by the same soil. It is evident that the relative oxidizing powers are not altered by inoculated sulfur.

Table 3 and figure 2 give a comparison between the total sulfur content, the sulfate content and the sulfur-oxidizing efficiency. The total sulfur analyses show that all soils except the muck soil 14 are low in total sulfur.

TABLE 2
Sulfification of flour sulfur vs. inoculated sulfur

SOIL NUMBER	SULFATES				AMOUNT OXIDIZED	
	Start*	Check	Flour sulfur	Inoculated sulfur	Flour sulfur	Inoculated sulfur
	p. p. m.	p. p. m.	p. p. m.	p. p. m.	per cent	per cent
1	15	50	1140	1032	36	33
2	22	68	1596	1200	51	38
3	27	52	876	1128	28	36
4	56	336	1848	2256	50	64
5	26	44	276	312	8	9
6	36	52	408	540	12	17
7	18	54	432	480	13	14
8	30	64	156	180	3	4
9	76	194	648	888	15	23
10	47	74	444	840	12	26
11	94	119	708	1176	23	35
12	496	648	948	948	10	10
13	25	34	100	140	2	4
14	239	444	2280	1876	61	48

* Sulfates in soil used for sulfification test.

The figures given are averages of triplicate determinations. No apparent relation exists between the total sulfur content and the sulfur-oxidizing power. An interesting fact is that the field application of sulfur to Umatilla sandy soil 2, and Stanfield fine sand 4, had little or no effect on the total sulfur content yet the sulfur-oxidizing power was stimulated by making the soil a favorable medium for the growth of the sulfur oxidizing bacteria. The sulfate content was higher in soil 4. This soil is not subject to extensive leaching like soil 2. In comparing soils 5 and 6, Salem clay loam, it will be seen that the field application of sulfur caused only a slight increase in the sulfur-oxidizing power and that the total sulfur and the sulfate content were not affected. This soil gave a remarkable increase in the yield of alfalfa when 100 pounds of sulfur was applied in 1915. This plot was sulfured again in 1917. Despite the low sulfur content of soil 7 (Medford loam) this soil has failed to show crop response when sulfur was added. This failure to respond cannot be due

to lack of sulfur bacteria. Antelope clay adobe (soil 8) always gives an enormous increase in the yield of alfalfa when sulfur is applied at 100 pounds per acre, yet the total sulfur is higher than the Medford loam and the sulfur-oxidizing power is less.

The fine sandy loam soils of Klamath County vary widely in their total sulfur content. Soil 9 was taken from an unsulfured area where no crop response to sulfur was apparent. This may be explained by the high sulfur content. Samples 10 and 11 from the Case ranch show little variation. The application of sulfur stimulated the sulfur-oxidizing power of soil 11 despite the lower total sulfur content.

The Willamette Valley soils 12 (Willamette silt loam) and 13 (Dayton silt loam) have a comparatively high total sulfur content and a low sulfur-oxidizing power. The low sulfur-oxidizing power especially in the Dayton silt loam is due to the fact that the soils are heavy, and it seems apparent that aeration

TABLE 3
Relation between total sulfur, sulfate content and sulfur oxidizing power

SOIL NUMBER	TOTAL SULFUR		SULFATE CONTENT	SULFUR OXIDIZED IN 14 DAYS
	<i>parts per million</i>	<i>per cent</i>	<i>parts per million</i>	<i>per cent</i>
1	55	0.006	14	28
2	55	0.006	18	39
3	145	0.015	21	21
4	110	0.011	115	38
5	155	0.016	25	7
6	135	0.014	23	10
7	80	0.008	18	11
8	110	0.011	24	2
9	235	0.024	64	11
10	144	0.014	42	9
11	110	0.011	94	16
12	274	0.028	526	7
13	164	0.016	21	2
14	780	0.078	296	36

is one of the most essential factors to sulfur oxidation. Sample 14 (muck) has a high sulfur-oxidizing power and a high total sulfur and sulfate content.

THE BUFFER VALUES OF THE SAMPLES STUDIED

Recently an article by Joffe and McLean (6) reported work along somewhat similar lines. The samples of soil used by them came from the southern Oregon region and with one exception were heavy soils. Some of these same soil types are used in this experiment along with soils of varying physical and chemical composition from three other regions. With the exception of samples 12, 13 and 14 these soils all came from semi-arid irrigated sections.

The sulfur used in this experiment was equivalent to one ton per acre. That this amount is excessive can easily be deduced from the previous mention that 100 pounds of sulfur per acre gives an increase of several hundred per cent on some of these soils when applied to alfalfa.

The ability of the heavy soils to neutralize the acidity formed through the oxidation of sulfur is shown in table 4, in which a comparison is made between

the original reaction and the reaction after four weeks of incubation. These soils are irrigated with water coming from mountains containing limestone and various salts of high buffer qualities which remove the possibility of any injurious accumulation of acids through the oxidation of nominal amounts of sulfur.

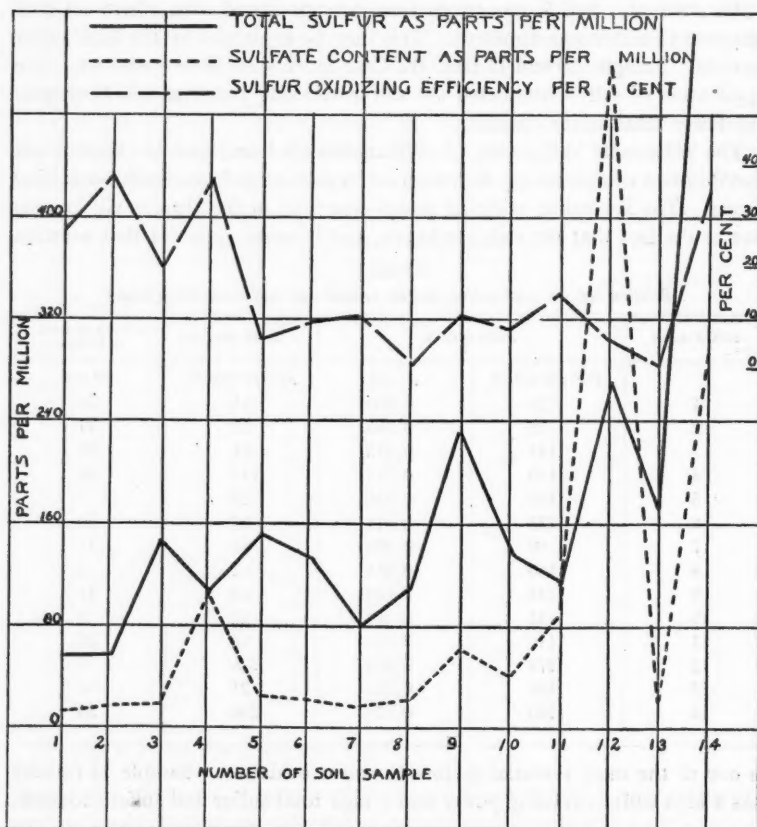


FIG. 2. SULFUR, SULFATES AND SULFUR-OXIDIZING POWER

Table 4 also points to the fact that inoculated sulfur is oxidized more rapidly than uninoculated sulfur. Since the value of sulfur when applied to alfalfa in Oregon lies in the fact that a limiting plant food element is being supplied and that all soils studied have a strong oxidizing flora, our data does not show any appreciable margin between the commercial values of the two forms.

There are slight discrepancies in the data presented in regard to reaction as well as to the yield of sulfates. This is to be expected. Variations in the compactness of the soils in the tumblers and wide experimental factors in the methods used can easily account for this.

TABLE 4
Buffer qualities of soils studied

SAMPLE NUMBER	TYPE OF SOIL	ORIGINAL REACTION	INCUBATED 1 MONTH						INCUBATED 2 MONTHS				INCUBATED 4 MONTHS				
			Flour sulfur*			Inoculated sulfur*			Flour sulfur*		Inoculated sulfur*		Flour sulfur*		Inoculated sulfur*		
			Reaction	SO ₄ per 100 gm. soil		Reaction	SO ₄ per 100 gm. soil		Reaction	SO ₄ per 100 gm. soil		Reaction	SO ₄ per 100 gm. soil		Reaction	SO ₄ per 100 gm. soil	
			pH	pH	mgm.	pH	mgm.		pH	mgm.		pH	mgm.		pH	mgm.	
1	Medium sand	7.2	6.0	57.1	6.0	100.0		6.2	100.0	5.4	80.0	5.0	261.0	5.0	375.0		
2	Medium sand	7.0	6.2	111.3	5.9	107.7		5.4	160.0	5.1	89.0	5.0	400.0	4.6	400.0		
3	Fine sand	7.1	6.0	76.9	5.9	66.7		5.8	80.0	5.9	80.0	4.6	300.0	4.6	500.0		
4	Fine sand	6.8	6.0	83.3	5.9	105.2		5.4	123.0	5.2	89.0	4.9	400.0	4.9	428.0		
5	Clay loam	6.4	6.0	66.7	5.9	100.0		6.4	89.0	5.9	89.0	5.5	333.5	5.5	400.0		
6	Clay loam	6.8	6.2	58.8	5.9	74.1		6.4	89.0	5.9	133.3	5.2	222.0	5.8	300.0		
7	Loam	6.9	6.4	66.7	5.8	74.1		6.0	42.1	6.2	160.0	5.0	500.0	5.6	222.0		
8	Clay adobe	6.7	6.6	26.2	5.9	43.5		6.8	45.7	6.6	80.0	6.2	286.0	6.4	318.0		
9	Sandy loam	6.2	6.1	41.2	5.9	47.1		6.4	40.0	6.0	48.8						
10	Sandy loam	6.4	6.2	33.2	6.0	57.2		6.4	40.0	5.9	84.3	5.6	272.5	5.8	300.0		
11	Sandy loam	6.4	6.4	100.0	5.5	107.7		6.6	177.8	6.3	84.3	5.2	375.0	5.8	400.0		
12	Silt loam	5.6	5.6	33.2	5.6	55.6		5.9	57.2	5.9	67.7	5.8	127.7	5.4	333.5		
13	Silt loam	5.8	5.9	28.6	5.9	6.2		5.9	32.7	6.2	29.6	5.0	158.0	4.8	153.7		
14	Muck	5.4	5.8	46.0	5.6	52.2		5.8	57.2	5.4	37.6	5.2	120.0	5.2	160.0		

*One hundred grams of sulfur used to each 100 gm. of soil in a glass tumbler.

CONCLUSIONS

1. All soils included in the investigation are capable of oxidizing sodium sulfide and flour sulfur. While there is considerable variation between soils in sulfur oxidizing efficiency all appear to be efficient enough to oxidize enough sulfur to supply the needs of starving plants within a comparatively short time.

2. A general relation exists between sulfofying power and sulfate content, curves representing these running more or less parallel.

3. No relation is apparent between total sulfur content and sulfofying power.

4. No relation exists between total sulfur content and sulfate content.

5. Application of sulfur to a soil tends to increase the sulfur oxidizing efficiency of that soil.

6. Inoculated sulfur stimulates sulfofication, but for the soils studied its need is not indicated.

7. Temperature and aeration are important factors affecting sulfofication, an increase in either tending to increase the rate of sulfur oxidation.

8. The buffer qualities of the soils studied are indicated by their change in hydrogen-ion concentration. The heavy soils show a remarkable ability to neutralize the acidity formed through the oxidation of sulfur. The soils

studied having high buffer value were heavy soils in which sulfur oxidation was slow compared to the light sandy soils of low buffer value.

9. No apparent relationship exists between the hydrogen-ion concentration and the sulfur oxidizing power of a soil.

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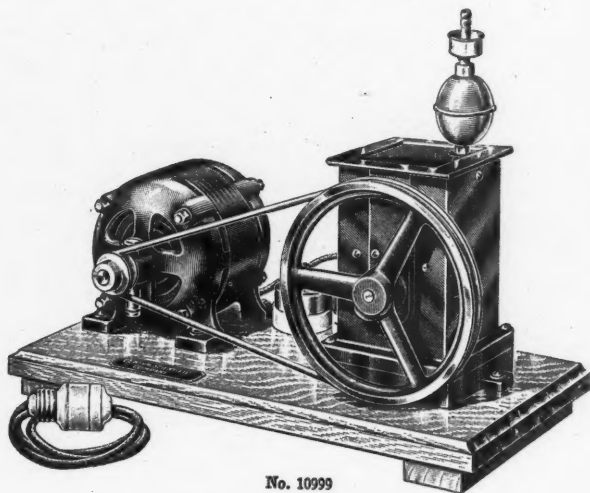
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